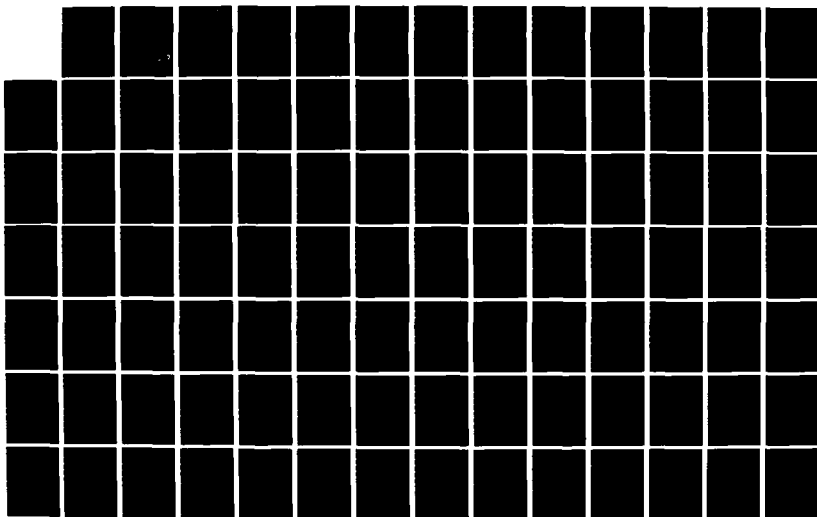


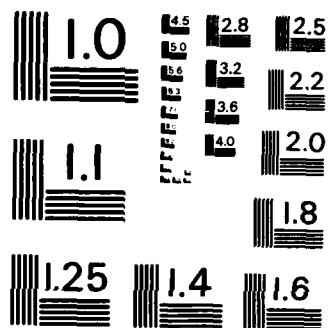
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AN EXPERIMENTAL EVALUATION OF THE EFFECTS  
OF SELECTED ORGANIC COMPOUNDS  
ON THE FORMATION OF INSOLUBLES IN DIESEL FUELS

By

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19. Abstract:

The nature of the base fuel was important in determining the amount of sediment formed in the presence of a given heterocompound. Of the nine compounds individually tested, 2,5-dimethylpyrrole (DMP) and 1,2,5-trimethylpyrrole produced the greatest amounts of sediment, and 2-methylpiperazine (MPPZ), 1-dodecanethiol (DDSH), and 2,6-di-tert-butylphenol the least. Also, DDSH over a range of concentrations showed a synergistic effect in the presence of a constant level of DMP. In contrast, MPPZ inhibited the formation of sediment in the presence of an equivalent concentration of DMP.

A number of sediment mass versus time curves gave evidence of an induction period. Curves of sediment mass versus compound concentration was roughly linear.

Recommendations for future work include continuing the use of DMP as a model sediment-former to study inhibition by other compounds; emphasizing the study of oxygen- and sulfur-containing compounds; developing methods to identify compounds such as DMP in typical fuels; investigating the properties of fuels to identify the source of different fuel responses to the same dosage of a heterocompound; studying MPPZ in fuels at ambient conditions to ascertain whether inhibition can be indefinitely maintained; and continuing the comparison of the available test methods to discover which are most useful in characterizing the stability of diesel fuels.

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# LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
atm	atmosphere
b.p.	boiling point
C	Celsius (temperature scale)
C	carbon
DDSH	1-dodecanethiol
DF	degrees of freedom
DFM	U. S. Navy Fuel Oil, Diesel, Marine (MIL-F-16884G; NATO symbol F-76)
DMP	2,5-dimethylpyrrole
DTNSRDC	David Taylor Naval Ship Research and Development Center, Bethesda, Maryland
F	Fahrenheit (temperature scale)
g	gram
H	hydrogen
hr(s)	hour(s)
HS	highly significant
JFTOT	Jet Fuel Thermal Oxidation Test (ASTM D3241 method)
JP-5	U. S. Navy aviation turbine fuel (MIL-T-5624; NATO symbol F-44)
K	potassium
L	liter
mg	milligram
ml	milliliter
mm	millimeter
m.p.	melting point
MPPZ	2-methylpiperazine
MS	mean square
MSR	mean square ratio
n	normal (as in "n-decane")
N	nitrogen
NATO	North Atlantic Treaty Organization
NS	not significant
O	oxygen

P	pressure or partial pressure
$\Delta P$	pressure gradient across test filter in ASTM D3241 (JFTOT)
PS	probably significant
r	correlation coefficient
R	Rankine (Fahrenheit absolute temperature scale, $R = 460 + F$ )
$\sigma$	(sigma) standard deviation
S	sulfur
sec	second
SS	sums of squares
t	time
T	absolute temperature
TAN	total acid number
TDR	tube deposit rating in ASTM D3241 (JFTOT)
tert-	(hyphenated prefix) tertiary
TMP	1,2,5-trimethylpyrrole
USNA	United States Naval Academy
wk(s)	week(s)
x	nitrogen reagent code (general)
X	fuel code (general)
yr(s)	year(s)

## ABSTRACT

The study documents and interrelates five experimental programs conducted by the David Taylor Naval Ship Research and Development Center in-house or under contract. The programs were designed to increase understanding of the effects of eleven selected heterocompounds on the stability of diesel-range fuels. The programs employed any or all of four different stability tests ranging from an oven test conducted at 150 F (65.6 C) for periods up to eight weeks to a test which exposed the fuel to a temperature of 500 F (260 C) for a few seconds. Ranking of the fuels and fuel mixes by all of the tests was reasonably consistent.

The nature of the base fuel was important in determining the amount of sediment formed in the presence of a given heterocompound. Of the nine compounds individually tested, 2,5-dimethylpyrrole (DMP) and 1,2,5-trimethylpyrrole produced the greatest amounts of sediment, and 2-methylpiperazine (MPPZ), 1-dodecanethiol (DDSH), and 2,6-di-tert-butylphenol the least. Also, DDSH over a range of concentrations showed a synergistic effect in the presence of a constant level of DMP. In contrast, MPPZ inhibited the formation of sediment in the presence of an equivalent concentration of DMP.

A number of sediment mass versus time curves gave evidence of an induction period. Curves of sediment mass versus compound concentration were roughly linear.

Recommendations for future work include continuing the use of DMP as a model sediment-former to study inhibition by

other compounds; emphasizing the study of oxygen- and sulfur-containing compounds; developing methods to identify compounds such as DMP in typical fuels; investigating the properties of fuels to identify the source of different fuel responses to the same dosage of a heterocompound; studying MPPZ in fuels at ambient conditions to ascertain whether inhibition can be indefinitely maintained; and continuing the comparison of the available test methods to discover which are most useful in characterizing the stability of diesel fuels.

## INTRODUCTION

Fuel instability is measured in terms of the amount of solids produced in storage. The production of such solids can seriously interfere with the use to which the fuel is put. For example, the solids could appear as particulates which might clog fuel orifices or filters, or they could show up as adherent gums or varnishes on heat exchanger tubes or other heated surfaces. Lower temperature storage conditions may over long periods result in the first kind of sediment; higher temperature conditions, the second. Thus, fuel stability is of importance to users of fuels.

The question of fuel stability is of vital concern to the Navy. The Navy must frequently store fuels under less than ideal conditions for long periods of time. Further, the Navy employs gas turbines and diesel engines which expose the fuel to high temperatures before it enters the combustion zone.

The compounds responsible for the production of sediment in fuels are of several classes. Perhaps the most common culprits are certain organic nitrogen compounds. In addition, various sulfur and oxygen compounds are implicated, especially with regard to the manner in which they may interact with some of the deleterious nitrogen compounds. Certain hydrocarbons, particularly unsaturated hydrocarbons, are also involved.

Nitrogen, sulfur, and oxygen compounds appear in appreciable concentrations in the heavy ends of petroleum as well



as in crudes from alternate sources (e.g., shale rock and coal). These facts are of special concern because, as high grade petroleum stocks dwindle, these less desirable materials will be used increasingly to prepare fuel oils.

This report documents five limited-objective studies conducted in 1931 and 1962. The first project, the Nitrogen Reagent Study, investigated the effect of eight nitrogen compounds on the stability of five different fuels. The second study, Interaction of a Pyrrole and a Thiol, measured the effect of adding 1-dodecanethiol, a sulfur compound, to a fuel containing 2,5-dimethylpyrrole (DMP), a nitrogen compound known to contribute strongly to fuel instability. The third study, Interaction of a Pyrrole and a Piperazine, investigated the effect of adding 2-methylpiperazine, a nitrogen compound, to a stable diesel fuel containing DMP. The fourth study, Concentration Effects of a Pyrrole, was concerned with the effect of the concentration of DMP on the mass of sediment formed. The fifth study, Screening of Nitrogen, Oxygen, and Sulfur Reagents, investigated the tendency of different nitrogen, oxygen, and sulfur compounds to form deposits when each is added singly to the fuel.

Four kinds of stability tests which differed primarily with respect to the duration and temperature of storage were used in these five studies. Different levels of oxygen exposure were also involved. Three measures of fuel stability were used. The first was the weight of the sediment obtained upon filtration and solvent extraction. The second was the optical density of the solids obtained by filtration. The third measure combined

the pressure gradient which developed across a test filter and the optical density of the deposit on a heated metal tube to estimate filterable insolubles and adherent gum, respectively.

The four stability tests are of two basic types: oven tests and higher temperature tests. Oven tests were conducted at 65.6 C (150 F), although the same type of test has been run by others at 43.3 C (110 F) and at 82.2 C (180 F). The higher temperature tests included ASTM Method D2274 (95 C or 203 F), a 150 C (302 F) test, and ASTM Method D3241 (the JFTOT test) which involves short exposure to a temperature of 260 C (500 F).

The goals of these five limited-objective studies were manifold. Some or all attempted

- (1) to ascertain the importance of the base fuel in insolubles formation
- (2) to compare four stability test methods through correlation of the results obtained
- (3) to determine which compounds among those tested produced the largest quantities of sediment, and which the least
- (4) to detect compound interactions that either increase or decrease total insolubles
- (5) to discover whether the formation of sediment by a particular compound (2,5-dimethylpyrrole) is a linear or nonlinear function of its concentration
- (6) to ascertain whether the mass ratio of two added

compounds (2,5-dimethylpyrrole and 1-dodecanethiol) is a critical factor in the formation of sediment

(7) to examine the relationship of sediment mass and time of storage for evidence of mechanism features such as an induction period

This report describes the various tests, presents the results of the experiments, and evaluates their implications. Only the results from the pyrrole-thiol interaction study, which was done under contract, have been previously documented. They are repeated in this report to provide a comparison and to round out the series of limited-objective experiments.

## TECHNICAL BACKGROUND

The stability of diesel-type fuels has been the object of investigation for a long time, but the fuel crisis of a decade ago spurred greatly renewed interest. Even a moderate shortage of petroleum crudes would require increased dependence on fuels from alternate sources (such as oil shale, coal, and tar sands) to make up the shortfall. Crudes from such sources have compositions which differ appreciably from typical petroleum crudes. In particular, the heteroatom proportions are distinctly different. Taylor and Hall<sup>(1)\*</sup> give the following composition ranges in crudes derived from petroleum, shale oil, and coal:

	<u>Petroleum</u>	<u>Shale Liquid</u>	<u>Coal Liquid</u>
Sulfur, %	0.6-6.0	0.6-3	0.3-2.0
Oxygen, %	0.5-5.0	6	7-11
Nitrogen, %	0.1-0.5	1-3	0.6-2.0

The presence of any of these three elements in the finished fuel can cause problems associated with performance, emissions, and stability.

Conditions of storage such as increased light, heat, and dissolved oxygen all contribute significantly to fuel instability. However, the presence of certain heterocompounds is the principal underlying cause of sediment formation which is the visible evidence of instability. The key elements in these heterocompounds are oxygen, sulfur, and nitrogen. A brief discussion of a few classes of these compounds follows.

---

\*A complete list of references is given on p. 71.

### Compounds of Oxygen and Sulfur

Most compounds of oxygen and sulfur (except sulfonic acids) do not contribute significantly to fuel instability when present in fuels by themselves. However, some oxygen compounds (such as carboxylic acids) interact synergistically with deleterious nitrogen compounds to increase the formation of sediment. Also, some sulfur compounds (such as aromatic thiols) may inhibit the process in the presence of the same nitrogen compounds<sup>(2)</sup>.

### Compounds of Nitrogen

Nitrogen compounds, which are found in higher concentration in shale- and coal-derived liquids than in petroleum crudes, are a major source of concern, for two reasons. First, some nitrogen compounds have a detrimental effect on fuel stability. Second, the catalytic hydrogenation usually employed to remove most of the nitrogen is difficult and adds considerably to processing costs.

The compounds which have proven most detrimental to fuel stability are alkylated heterocyclic nitrogen compounds. Of these, the most reactive are compounds containing two or more alkyl groups, at least one of which is attached to a carbon adjacent to the nitrogen<sup>(2)</sup>. A key compound in this category is 2,5-dimethylpyrrole (DMP). Basic nitrogen compounds such as amines and amides are not harmful by themselves. However, some of these species may increase or decrease sedimentation by interaction with deleterious nitrogen compounds. Fusion of an aromatic ring to the hetero ring generally reduces activity, so that indoles are less harmful than pyrroles<sup>(3)</sup>.

### Mechanisms of the Fuel Sedimentation Reaction

Johnson and Goldfein<sup>(4)</sup> have reviewed the literature relating to mechanisms of deposit formation. They report that most studies suggest hydroperoxide formation as the initial step in the reaction sequence. However, two investigators<sup>(5,6)</sup> agree that deposit-forming reactions are merely minor side reactions to the main reaction sequence which produces large amounts of soluble oxygenated compounds. The reactions following hydroperoxide formation are speculative because of the great complexity of the sediment produced. Frankenfeld and Taylor<sup>(3)</sup> propose that sediment results from an oxidative condensation of nitrogen heterocycles to yield low molecular weight polymers of two, three, or four monomer units (oligomers). When a compound such as DMP is involved, bonds holding the chains together are formed between the methyl carbons attached to the hetero rings. Because of the key role of the hydroperoxide group, dissolved oxygen appears necessary for the sediment-forming reaction to proceed at an appreciable rate.

### The Role of the Base Fuel

The amount of sediment formed in a fuel containing deleterious compounds increases as the fuel increases in complexity. That is, the order of increasing instability in fuels containing DMP would be n-decane < jet fuel < No. 2 diesel fuel. Interactive effects of two or more sensitive compounds increase in the same order. Frankenfeld and Taylor<sup>(3)</sup> suggest that the effects observed are caused by trace impurities in the less highly refined fuels.

### Temperature Equivalence in Sedimentation Reactions

Fuels can be tested in a manner closely approaching typical field storage by using a variety of test containers to store fuels at ambient temperatures under typical atmospheric conditions. Such testing has the disadvantage of requiring long periods of storage, perhaps as much as three years, to simulate actual storage conditions.

Garner and White<sup>(7)</sup> were able to correlate results of accelerated storage in beakers at 43 C (110 F) with storage at the effective annual temperature of 19 C (67 F) for vented bottle storage at Annapolis. They confirmed that one week's storage at the higher temperature was equivalent to a month's storage at the lower temperature.

An Arrhenius-type equation developed by Nixon and Cole<sup>(8)</sup> was an attempt to quantify the concept of equivalency of storage conditions. In its original form the equation relates any two sets of equivalent storage conditions (temperature, time, and partial pressure of oxygen). If the values 67 F (527 R), 3 years (26,300 hours), and 0.20 atmosphere, which are the conditions for ambient storage in the Garner-White study, are substituted for one set of conditions, the Nixon-Cole equation becomes

$$\log t + 0.52 \log P = (4500/T) - 4,482$$

The solid line in Figure 1 is the plot of this curve;  $t$  = storage time (hours),  $P$  = partial pressure of oxygen (atmospheres), and  $T$  = Rankine temperature ( $R = 460 + F$ ). Any of the three variables may be calculated if the other two values are

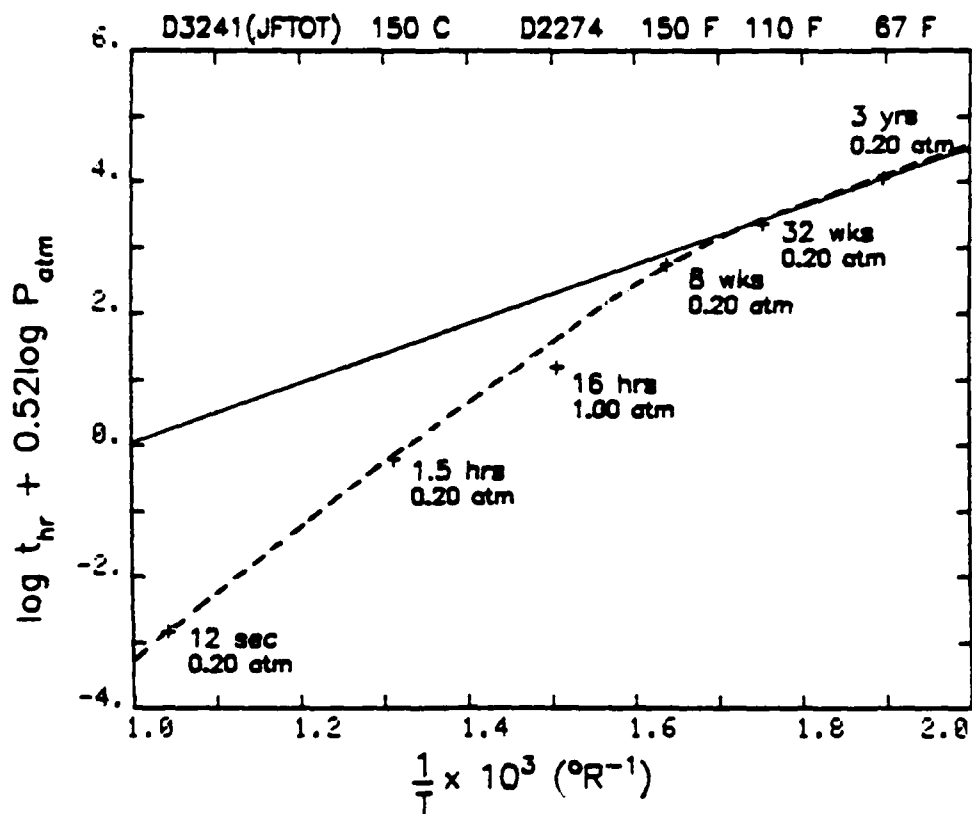


Figure 1 - Nixon-Cole equation and stability test conditions.



known.

Figure 1 shows the storage conditions (indicated by symbols "+") for six fuel stability tests identified at the top of the figure as D3241 (JFTOT), 150 C, D2274, 150 F, 110 F, and 67 F. The first four are tests used in the current studies and are described elsewhere in this report. The last two (used in the Garner-White study<sup>(7)</sup>) are similar to the 150 F test except that the 67 F test does not require oven storage. The points for the first three (higher temperature) tests do not fall on the Nixon-Cole curve and should not therefore represent conditions equivalent to those of the last three tests. However, experience has shown that the sedimentation produced in the 150 C and D2274 tests is roughly equivalent to that produced in 150 F and 110 F tests. Thus, the Nixon-Cole curve may not be the locus of all equivalent storage conditions. Since the break occurs between the 150 F and D2274 (203 F) test conditions it appears that the Nixon-Cole relation is not valid for conditions much more severe than 150 F for 6 weeks under 0.20 atmosphere partial pressure of oxygen. The most logical reason for this is a change in the mechanism of sedimentation which may occur as the temperature increases. The postulated change in mechanism requires less exposure time than that predicted by the Nixon-Cole equation for temperatures above 150 F.

A more complex equation than Nixon-Cole, such as an equation for the dashed curve in Figure 1, might accommodate all presumably equivalent test conditions from 3 years at 67 F to a few seconds at 500 F (JFTOT conditions). Although inclusion of the

D.274 (203 F) and 150 C (302 F) test conditions within the scope of the new equation might be justified, experience has shown that predictions of the JFTOT test do not uniformly match those of other tests. Since the JFTOT measures effects which are different than those of other tests, comparing the results is not straightforward. The dashed curve, then, is merely speculative.

Accelerated tests thus have their limitations. Extrapolation of low-temperature results to higher temperatures (or vice versa) may be fraught with uncertainty. Whether lower or higher temperature tests are used should depend not only on the usual conditions of storage but also on conditions that the fuel may encounter in use. For example, jet fuels may be in contact with elevated surface temperatures for short periods before entering the combustion zone. A short-duration, high-temperature test such as the JFTOT is therefore appropriate.

## TEST METHODS USED IN STABILITY STUDIES

The salient features of the four test methods used to determine the stability of the fuels and fuel-reagent mixtures in the studies reviewed in this report are listed in Table 1. The conditions for the different methods range from storage up to 8 weeks at 150 F (65.6 C) to a residence time of approximately 12 seconds at 500 F (260 C). The methods also employ different degrees of exposure to oxygen.

The conditions of the tests as stated in Table 1 are those used in the current studies. In some of the standard methods these conditions may be adjustable parameters. For example, in ASTM D3241 (JFTOT) the storage (test section) temperature can be varied above and below 260 C. Also, in the 150 C test, the storage duration may be 160 minutes instead of 90 minutes.

TABLE 1  
FUEL STABILITY TEST METHODS

Method Title	Fuel Holder	Volume of Fuel	Heat Source	Storage Temperature	Storage Duration	Partial Pressure of Oxygen	Data Retrieved
ASTM D3241 Thermal Oxidation Stability of Aviation Fuels (JFTOT Procedure)	Metal bomb with screw cap	600 ml maximum	Electric resistance heating	260 C (500 F)	About 12 seconds in heated test section of metal tubing	0.20 atm maximum	Pressure drop across filter and optical density of deposit on heater tube by visual comparison with ASTM color standard or by Alcor Tube Deposit Rater
150 C Test High Temperature Stability of Distillate Fuels	25 X 200 mm Pyrex test tubes, open at top	50 ml	Oil bath	150 C (302 F)	90 minutes	0.20 atm maximum	Optical density of filter pad using reference blotter comparison or reflectance meter readings
ASTM D2274 Oxidation Stability of Distillate Fuel Oil (Accelerated Method)	45 X 600 mm Pyrex test tubes, loose glass wool plug	350 ml	Oil bath	95 C (203 F)	16 hours	1.00 atm (oxygen gas bubbled through)	Mass of filterable insolubles, adherent gum, and total insolubles expressed as mg/100 ml of fuel
150 F Test Test for Distillate Fuel Storage Stability	600 ml Wheaton bottles, vented	500 ml	Oven	65.6 C (150 F)	Various periods, from 1 day to 8 weeks	0.20 atm maximum	Mass of filterable insolubles, adherent gum, and total insolubles expressed as mg/100 ml of fuel

## FUELS AND REAGENTS

### Fuels

Brief descriptions and codes for five diesel- and jet-type fuels are presented in Table 2. All of these fuels were used in the Nitrogen Reagent Study, but only fuel A was used in the other four studies described in this report. For fuels A, C, and E, values of total acid number (TAN) are included.

### Reagents

Eleven nitrogen, sulfur, and oxygen compounds, from classes identified as possible constituents of diesel-range fuels, served as reagents in the stability studies reported herein. The names, codes, and other pertinent data for the eleven reagents are listed in Table 3. Structures of the compounds are shown in Figure 2.

### Reagent Mixture "m"

In the Nitrogen Reagent Study most of the tests required addition to the fuel of a mixture of eight nitrogen reagents. The mixture, coded "m", provides one liter of fuel with 260 mg of nitrogen, divided among the reagents as follows:

#### Reagent Mixture "m"

<u>Code</u>	<u>Nitrogen Compound</u>	<u>Nitrogen Contribution mg/liter of fuel</u>
f	pyrrole	40
g	2,5-dimethylpyrrole	40
h	1,2,5-trimethylpyrrole	40
i	2-methylindole	40
j	2-methylpiperazine	40
k	quinaldine	40
l	7-azaindole	20
n	3-methylpyridazine	20
		<u>20</u>
		Total... 260

TABLE 2  
FUELS USED IN STABILITY STUDIES

<u>Fuel Code</u>	<u>Description</u>	<u>TAN<sup>a</sup></u>
A	Shale-Derived Diesel Fuel	0.03
B	JP-5, Long Beach Annex NSB, San Diego, CA	----
C	Diesel Fuel, Marine, from a European Refinery	0.02
D	No. 2 Diesel Fuel containing additives, from a U.S. Refinery	----
E	Shale-Derived Jet Fuel	0.01

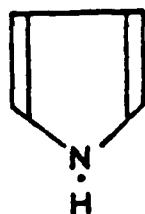
<sup>a</sup>Total Acid Number, mg KOH/g

TABLE 3

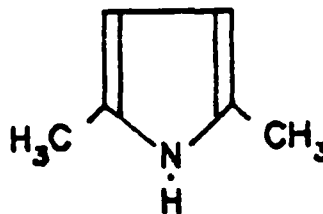
## DESCRIPTIVE PROPERTIES OF REAGENTS SELECTED FOR STUDY

Reagent Code	Name of Reagent (Abbreviation)	Formula Weight	State (m.p., C)	b.p., C	Specific Gravity
f	pyrrole	67.09	liquid (-23)	131	0.967
g	2,5-dimethyl-pyrrole (DMP)	95.15	liquid	165 (740 mm)	0.935
h	1,2,5-trimethyl-pyrrole (TMP)	109.17	liquid	173	0.807
i	2-methylindole	131.18	solid (58-60)	273	.....
j	2-methylpiperazine (MPPZ)	100.17	solid	155 (763 mm)	.....
k	quinaldine	143.19	liquid (-2)	248	1.058
l	7-azaindole	118.14	solid (105-107)	...	.....
n	3-methylpyridazine	94.12	liquid	214	.....
q	isoquinoline	129.16	solid (26-28)	242	1.099
O-1	2,6-di-tert-butylphenol	206.33	solid (35-38)	253	.....
S-1	1-dodecanethiol (DDSH)	202.40	liquid	266-283	0.845

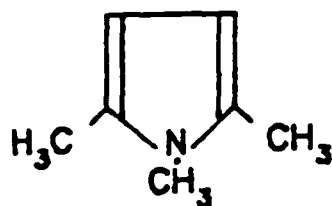
f pyrrole



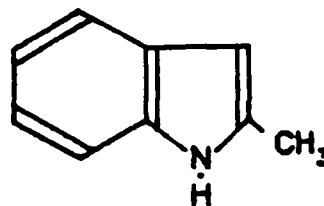
g 2,5-dimethylpyrrole



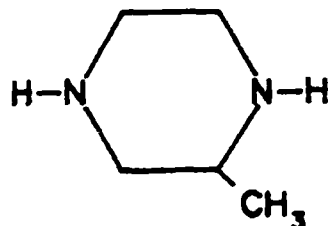
h 1,2,5-trimethylpyrrole



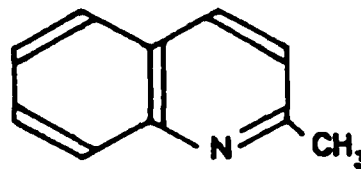
i 2-methylindole



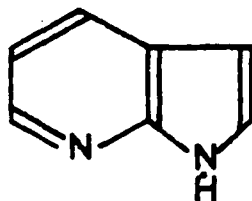
j 2-methylpiperazine



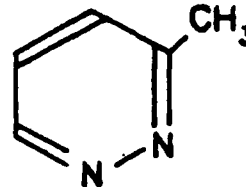
k quinaldine (2-methylquinoline)



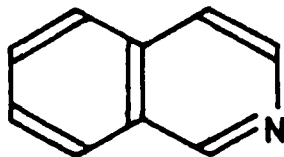
l 7-azaindole



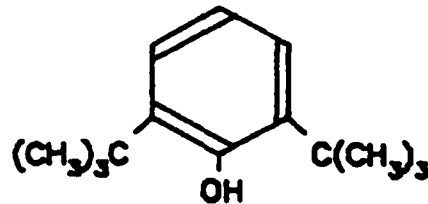
n 3-methylpyridazine



q isoquinoline



0-1 2,6-di-tert-butylphenol



S-1 1-dodecanethiol



Figure 2 - Reagent codes, names, and structures



### Fuel-Reagent Mixture Codes

A sample of fuel D containing the appropriate amount of the nitrogen reagent mixture m is coded "Dm" and contains 280 mg of nitrogen per liter in addition to any nitrogen originally present in D. Similarly, a code "Amj<sup>2</sup>" would mean fuel A plus mixture m plus 80 (2 X 40) mg extra nitrogen in the form of additional reagent j; this mix contains a total of 360 mg of added nitrogen per liter. Finally, the code "Amg<sup>2</sup>i<sup>2</sup>k<sup>2</sup>" means fuel A plus mixture m plus additional reagents g, i, and k, each at a level sufficient to add 80 mg of nitrogen (providing a total of 280 + 240 = 520 mg of added nitrogen per liter).

## EXPERIMENTAL PROGRAM

A number of limited-objective projects have been conducted by DTNSRDC in-house or under contract to increase understanding of the effects of heterocompounds on the stability of diesel-range fuels. The compounds selected could feasibly be present either in petroleum or in alternative diesel fuels or in both. The compounds were tested in a stable base fuel singly or in various combinations. Analyses of the base fuel indicated initial nitrogen concentrations of the order of 30 mg/liter. Concentrations of added heterocompounds provided from 0 to 1500 mg nitrogen/liter and up to 858 mg oxygen or sulfur/liter. The test methods provided a range of stressing temperatures from 150 F (65C) to 500 F (260 C) and a range of stress times from 12 seconds (at 500 F) to 8 weeks (at 150 F).

Brief statements regarding the goals and approaches of the five projects (A through E) follow. Table 4 contains additional details in the form of the specific stability tests and objectives for each project.

### A. Nitrogen Reagent Study

- Goal: To test the effects of nitrogen compounds on the stability of five fuels.
- Approach: The fuels were tested neat or mixed with a set proportion of eight nitrogen compounds. For ten of the fuel mixes triple concentrations of from one to three of the nitrogen compounds were used in the added eight-component nitrogen mix.

TABLE 4  
DESCRIPTION OF EXPERIMENTAL STUDIES REVIEWED

<u>Study Title</u>	<u>Stability Tests Used</u>	<u>Objectives</u>
A. Nitrogen Reagent Study	ASTM D2274 ASTM D3241 (JFTOT)* 150 C 150 F (2,4,6 weeks)	(1) Ranking of 6 nitrogen compounds (2) Role of the base fuel (3) Rating of test methods (4) Time effects
B. Interaction of a Pyrrole and a Thiol	150 F (1,2,4,8,11,17 days)	(1) Interaction of a nitrogen compound with a sulfur compound (2) Effects of sulfur/nitrogen ratio (3) Time effects
C. Interaction of a Pyrrole and a Piperazine	ASTM D2274 ASTM D3241 (JFTOT)* 150 C 150 F (3 days; 1,2,4,8 weeks)	(1) Interaction of two nitrogen compounds (2) Time effects
D. Concentration Effects of a Pyrrole	ASTM D2274 ASTM D3241 (JFTOT)*	(1) Concentration effects of 2,5-dimethylpyrrole
E. Screening of Nitrogen, Oxygen, and Sulfur Reagents	ASTM D2274 ASTM D3241 (JFTOT)*	(1) Interaction of 5 nitrogen compounds, 1 sulfur compound, and 1 oxygen compound with the base fuel (2) Critical compounds (3) Temperature effects

\*JFTOT = Jet Fuel Thermal Oxidation Test

#### B. Interaction of a Pyrrole and a Thiol

Goal: To determine whether a particular thiol, 1-dodecanethiol, has a positive or negative effect on the formation of insolubles in a fuel containing 2,5-dimethylpyrrole, and to determine whether the sulfur/nitrogen mass ratio is critical.

Approach: The pyrrole was used at 750 mg nitrogen/liter in all samples. The thiol was used to provide sulfur at sulfur/nitrogen mass ratios of 0, 0.25, 0.67, 1.50, and 4.00.

Note: The work for this project was performed and previously documented by ARTECH Corporation, Falls Church, VA.

#### C. Interaction of a Pyrrole and a Piperazine

Goal: To determine whether there is an interaction between 2,5-dimethylpyrrole and 2-methylpiperazine in the formation of insolubles in fuel.

Approach: The data were assembled in a 2 X 2 factorial form, requiring testing of the neat base fuel and the base fuel plus the pyrrole alone, the piperazine alone, and the pyrrole plus the piperazine. In the ASTM D3241 test, the concentration was 100 mg nitrogen/liter for each nitrogen reagent present. In the other three tests (ASTM D2274, 150 C, and 150 F) the concentration of each reagent was 375 mg nitrogen/liter.

#### D. Concentration Effects of a Pyrrole

Goal: To ascertain whether the formation of insolubles is a linear function of the concentration of 2,5-dimethylpyrrole.

Approach: The concentration of the pyrrole was studied at 0, 93.75, and 375 mg nitrogen/liter in the ASTM D3241 test and at 0, 93.75, 187.5, 375, 750, and 1500 mg nitrogen/liter in the ASTM D2274 test.

### E. Screening of Nitrogen, Oxygen, and Sulfur Reagents

Goal: To screen a number of compounds to ascertain which ones are particularly likely to produce insolubles in fuel.

Approach: The reagent 2-methylpiperazine was tested in the ASTM D3241 test at 375 mg nitrogen/liter. The reagents 2,5-dimethylpyrrole, 2-methylindole, 2-methylpiperazine, isoquinoline, 1,2,5-trimethylpyrrole, 1-dodecanethiol, and 2,6-di-tert-butylphenol were tested by ASTM D2274 at 375 mg nitrogen/liter, 428 mg oxygen/liter, and 858 mg sulfur/liter (depending on the compound).

## RESULTS

The results of the five stability studies reviewed in this report are presented in Appendices A-E.

Appendix A (Nitrogen Reagent Study) records the results of the ASTM D3241 (JFTOT) test (Table A-1), the 150 C and ASTM D2274 tests (Table A-2), and the 150 F test (Table A-3). Table A-1 also identifies the fuels used and the composition of the reagent mixtures added.

Appendix B (Interaction of a Pyrrole and a Thiol) reports the filterable insolubles (Table B-1), adherent gum (Table B-2), total insolubles (Table B-3), and average rate of formation of total insolubles (Table B-4), for the 150 F test for each time period and each sulfur/nitrogen mass ratio.

Appendix C (Interaction of a Pyrrole and a Piperazine) reports the results of the ASTM D3241 (JFTOT) test (Table C-1), the ASTM D2274 test (Table C-2), the 150 C test (Table C-3), and the 150 F test (Table C-4). All the results of this study are presented in 2 X 2 factorial form. That is, there are four results recorded for each replicate at each test condition in each test method: base fuel with no added reagent, with the pyrrole added, with the piperazine added, and with both the pyrrole and the piperazine added.

Appendix D (Concentration Effects of a Pyrrole) reports the data for the base fuel and for two concentrations of the pyrrole in the ASTM D3241 (JFTOT) test (Table D-1) plus the three types of sediment mass for six concentrations of the pyrrole in the

ASTM D2274 test (Table D-2).

Appendix E (Screening of Nitrogen, Oxygen, and Sulfur Reagents) presents the ASTM D3241 (JFTOT) data for the base fuel and for one concentration of 2-methylpiperazine Table E-1) and the ASTM D2274 data for base fuel and for seven nitrogen, sulfur, and oxygen reagents (Table E-2).

## DISCUSSION OF RESULTS

### A. Nitrogen Reagent Study

Table 5 ranks all the fuels and fuel mixes in this study in the order of increasing sedimentation. In the D2274 and 150 F tests a higher rank means the fuel produces more insolubles. In the JFTOT and 150 C tests a higher rank means that some other measure of instability indicates greater instability (whether the numerical value is higher or lower is not important). The right-hand column of the table, "Overall Rank on 6 Tests", was obtained by ordering the ranks calculated from the average of the values in columns 2 to 7 for each fuel or mix. These ranks provide a measure of the relative sediment-producing tendencies of the five base fuels (A to E, inclusive) and the six nitrogen reagents f, g, h, i, j, and k. In the discussion, references to the total insolubles values in Tables A-2 and A-3 will be made in order to make evaluations more quantitative. The discussion will consider the ranking of the six nitrogen reagents, the role of the base fuel, comparison of the results of the different test methods, and time-total insolubles relationships.

### Ranking the Reagents

The overall rankings of the mixture  $Amx^2$  ( $x = f, g, h, i, j, k$ ) are, respectively, 9, 17, 20, 10, 6, 8. That is, the order for increasing sedimentation produced by adding extra reagent (80 mg N/L) to the mix  $Am$  is  $j < k < f < i \ll g < h$ . In this order, the rank differences  $Amx^2 - Am$  are -1, 1, 2, 3, 10, 13. This suggests that j (2-methylpiperazine) is the only reagent in the group



TABLE 5  
TEST RANKINGS OF TWENTY FUELS OR FUEL MIXES  
IN THE ORDER OF INCREASING INDEX OF SEDIMENTATION<sup>a</sup>

Fuel or Mix <sup>b</sup>	T E S T   P R O C E D U R E						Overall Rank on 6 Tests
	JFTOT	150 C	D2274	150 F 2 wks	150 F 4 wks	150 F 6 wks	
A	3	1	2	2	1	2	2
B	2	4	2	2	4	3	3
C	4	10	4	5	3	4	5
D	5	3	5	4	6	5	4
E	1	2	1	1	1	1	1
Am	6	9	7	12	9	6	7
Bm	17	11	13	9	8	9	11
Cm	18	20	15	15	14	12	16
Dm	20	19	19	14	15	16	19
Em	19	18	11	13	7	8	13
Amf <sup>2</sup>	12	13	8	7	12	11	9
Amg <sup>2</sup>	15	17	14	17	16	17	17
Amh <sup>2</sup>	16	16	18	16	20	20	20
Ami <sup>2</sup>	13	6	10	8	13	14	10
Amj <sup>2</sup>	9	4	6	6	5	7	6
Amk <sup>2</sup>	10	8	9	10	10	10	8
Amg <sup>2</sup> i <sup>2</sup>	8	12	20	19	19	15	14
Amg <sup>2</sup> k <sup>2</sup>	11	14	17	20	17	18	18
Ami <sup>2</sup> k <sup>2</sup>	14	7	12	11	11	13	12
Amg <sup>2</sup> i <sup>2</sup> k <sup>2</sup>	7	15	16	18	18	19	14

<sup>a</sup>Basis of rankings: Data in Table A-1, A-2, A-3. JFTOT: Spun TDR or Time for ΔP to reach 125 mm; 150 C: Average reference blotter numbers for the two trials; D2274 and 150 F: Total Insolubles.

<sup>b</sup>For explanation of symbols see Tables 2, 3, and A-1.

which has a negative impact on sediment formation. Piperazines are basic, so this behavior agrees with earlier reports<sup>(2)</sup> that basic compounds are either inactive or beneficial relative to sediment formation. In fact, amines and basic azides are used as oxidation inhibitors in lubricants and hydraulic fluids.

If the effect on the rankings of adding each component of a mixture is additive, as is implicit in the differences  $Am_x^2 - Am_y^2$  just cited, then it should also be possible to use the expressions  $Am_x^2 y^2 - Am_y^2$  in a similar way. Here the values for the two terms were taken from the overall rank column in Table 5:

<u>x</u>	<u>y</u>	<u><math>Am_x^2 y^2 - Am_y^2</math></u>	<u>Average Rank Difference</u>
g	none	10	
g	i	4*	10
g	k	10	
<hr/>			
i	none	3	
i	g	-3*	3.5
i	k	4	
<hr/>			
k	none	1	
k	g	1	1.3
k	i	2	

\*The overall rank (14) for  $Am_g^2 i^2$  in Table 5 is questionably low; the starred values were deleted from the averages in the right-hand column above.

The consistency of the two values for g, the two for i, and the three for k is sufficient to indicate that the assumption of additivity is roughly correct. The values represent the increase in rank contributed when 80 mg nitrogen per liter is added in the form of the specified reagent. Thus, reagent g (2,5-dimethylpyrrole) produces an increase in rank of about 10,

whereas reagent i (2-methylindole) and k (quinaldine) cause increases in rank of only 3 or 4 and 1 or 2, respectively, when added at the same nitrogen level.

If the total insolubles data recorded in Tables A-2 and A-3 for the D2274 test and the 150 F test (at 2, 4, and 6 weeks) are used to calculate  $x = (Amx^2 - Am)/2$ , the values shown in Table 6 are obtained. In this application the values of x represent the increase in total insolubles (in mg/100 ml) produced by adding 40 mg nitrogen/liter in the form of the specified reagent. The sum of the respective values of x shown in the right-hand column of Table 6 can be used to reevaluate the relative tendency of

TABLE 6  
NET TOTAL INSOLUBLES FOR SIX NITROGEN REAGENTS

$$x = (Amx^2 - Am)/2, \text{ mg/100 ml}$$

Reagent*	D2274	150 F 2 weeks	150 F 4 weeks	150 F 6 weeks	SUM
f	0.41	-----	1.96	4.79	-----
g	5.66	7.36	19.95	27.72	60.69
h	8.73	5.39	24.06	34.25	72.43
i	0.78	-1.65	2.21	6.50	7.84
j	-1.90	-1.83	-4.89	0.39	-8.23
k	0.77	-0.51	1.62	2.16	4.04

\*at 40 mg nitrogen/liter

the six tabulated reagents to produce sediment. The result is again  $j < k < f < i \ll g < h$  (rating f on all but the 2-week 150 F test result). Thus, both the ranks on four general methods and the sum of the total insolubles on two of them yield the same order, and both approaches suggest that only j (2-methylpiperazine) has inhibitory characteristics. The JFTOT results for  $Am_j^2$  versus  $Am$  show that short exposure to 500 F wipes out the inhibitory effect (see Table A-1).

#### Role of the Base Fuel

Based on the overall ranks in the right-hand column of Table 5, the order of increasing tendency to produce sediment or gum in the neat fuels is  $E < A < B < D < C$ . However, C and D exchange places if the ordering is done using the sum of the deposits in Table 7, which lists the total insolubles for the neat fuels and for the fuels treated with the reagent mixture m. The stability order of the fuels based on the sum of the total insolubles in the right-hand column becomes  $E < A < B < C \ll D$ ; not only have C and D exchanged places but the quantity of sediment produced in D is much greater than that in C. That fuel D does not have the stability of the other four is not surprising since it is a No. 2 diesel fuel which does not have to meet the more stringent requirements of a JP-5 (such as B), or even of a DFM, (such as C). The other two fuels, A and E, are diesel and jet fuels, respectively, which were prepared by extensive processing of shale oil stocks.

The sum of the total insolubles for the mixtures  $X_m$  (lower portion of Table 7) yields  $Am < Bm < Em \ll Cm \ll Dm$  as the instabili-

TABLE 7  
TOTAL INSOLUBLES FOR FIVE FUELS  
mg/100 ml

Fuel or Mix	D2274	150 F 2 weeks	150 F 4 weeks	150 F 6 weeks	SUM
A	0.9	0.5	0.3	1.1	2.8
B	0.9	0.6	0.9	1.3	3.7
C	1.3	1.0	0.9	1.5	4.7
D	1.8	0.7	3.6	21.	27.
E	0.8	0.2	0.3	0.7	2.0
Am <sup>a</sup>	3.7	14.	33.	42.	93.
Bm	8.2	11.	30.	45.	94.
Cm	17.	21.	41.	52.	131.
Dm	22.	21.	57.	75.	175.
Em	6.7	19.	25.	44.	95.
m <sup>b</sup>	10.	17.	36.	47.	110.

<sup>a</sup> "m" represents a mixture of eight nitrogen reagents: f,g,h,i, j, and k at 40 mg nitrogen/liter each; l and n at 20 mg nitrogen/liter each. Reagent symbols are identified in Table 3.

<sup>b</sup> average of five values  $X_m - \bar{X}$ .

ty order. Fuel C, the DFM, interacts more strongly with the nitrogen compounds than A, B, or E, but does not match the sediment production of D, so falls between the two groups. That both C and D produce considerably more insolubles than A, B, and E makes it very clear that the nature of the fuel plays an important role in the sediment-forming process. Frankenfeld and Taylor<sup>(3)</sup> state that sediment formation increases as the diluent becomes more complex, as, for example, in the order n-decane <

jet fuel < No. 2 diesel fuel. They claim, however, that the observed effects are apparently not due to the gross hydrocarbon composition or solvent effects but are caused by trace impurities which are present in less highly refined fuels. Trace impurities which could have this much effect are often metallic. Analysis for such contaminants might yield interesting results.

#### Comparison of Test Methods

It is possible to compare the stability tests with each other to arrive at an internal rating system by using the ranks in Table 5 as a basis and summing up the deviations of each method from the overall rank (right-hand column of the table) for each of the tests of the 20 fuels or mixes. The mean deviation for each test is then determined by dividing the sum of the deviations by 20. When this is done, one obtains:

Stability Method	Sum of Deviations in 20 Tests	Mean Deviation
-----	-----	-----
D2274	24	1.20
150 F - 6 wks	33	1.65
150 F - 2 wks	36	1.80
150 F - 4 wks	44	2.20
150 C	46	2.30
D3241 (JFTOT)	59	2.95
-----	-----	-----

Inspection of the mean deviations shows that the D2274 method departs the least from the mean of all the results while the JFTOT deviates the most. This outcome may be due to the fact that the D2274 temperature (203 F) and duration (16 hours) are neither the lowest nor the highest, while the JFTOT temperature

(500 F) and duration (about 12 seconds) are certainly extreme values. The reason for the order of the three 150 F time periods is not clear; perhaps the normal variations encountered in using this method make the result fortuitous.

Close comparison of the other methods with the D2274 test using actual test data (rather than Table 5 ranks) is probably not feasible for any except the 150 F test. This is because only the D2274 and 150 F tests report the same type of results, sediment mass. In Table 3 the total insolubles for these two tests are averaged for certain groups of fuels and fuel mixes. These are listed in the order of increasing total insolubles in the D2274 test.

Table 8 also shows the correlation coefficient "r", a measure of the degree of association between two variables. Its numerical value equals the ratio of the explained variation between the variables to the total variation (the sum of the explained and unexplained variations)<sup>(9)</sup>. The explained variation between two variables is that which results from an assumed functional dependence of one variable on the other; the unexplained variation results from experimental error. Values of "r" fall between +1 and -1 with +1 indicating a perfect correlation between the variables (no unexplained variation) and -1 indicating a perfect inverse or negative correlation. An r-value of zero indicates no correlation is likely; there is no functional dependence of the one variable on the other<sup>(10)</sup>.

Thus, in Table 8, the 6-week results are seen to yield the best correlation ( $r = 0.93$ ), as would be expected from the rank

TABLE 8  
COMPARISON OF AVERAGE TOTAL INSOLUBLES FOR TWO METHODS  
(D2274 and 150 F Tests)

mg/100 ml

<u>Fuels or Mixtures Averaged</u>	<u>D2274</u>	-----150 F Test-----		
		<u>2 weeks</u>	<u>4 weeks</u>	<u>6 weeks</u>
A,B,C,D,E (neat fuels)	1.2	0.6	1.2	5.2
Amj <sup>2</sup>	1.8	10.	23.	43.
Am	3.7	14.	33.	42.
Amf <sup>2</sup> , Ami <sup>2</sup> , Amj <sup>2</sup> , Amk <sup>2</sup>	4.3	11.*	30	49.
Em	6.7	20.	25.	44.
Amk <sup>2</sup> , Amg <sup>2</sup> k <sup>2</sup> , Ami <sup>2</sup> k <sup>2</sup> , Amg <sup>2</sup> i <sup>2</sup> k <sup>2</sup>	13.	30.	57.	76.
Bm, Cm, Dm, Em	14.	18.	38.	54.
Ami <sup>2</sup> , Amg <sup>2</sup> i <sup>2</sup> , Ami <sup>2</sup> k <sup>2</sup> , Amg <sup>2</sup> i <sup>2</sup> k <sup>2</sup>	14.	24.	58.	70.
Amg <sup>2</sup> , Amh <sup>2</sup>	18.	27.	77.	104.
Amg <sup>2</sup> , Amg <sup>2</sup> i <sup>2</sup> , Amg <sup>2</sup> k <sup>2</sup> , Amg <sup>2</sup> i <sup>2</sup> k <sup>2</sup>	19.	39.	77.	92.
-----				
D2274 versus 150 F				
Correlation Coefficients	----	0.89	0.91	0.93

\*This average does not include Amf<sup>2</sup> because filtration of the filterable insolubles was incomplete after three hours

deviation comparison. The 4-week result,  $r = 0.91$ , and the 2-week result,  $r = 0.89$ , indicate good agreement, but are a bit lower than would be expected for two methods which report the same kind of data. The significance of the three  $r$  values becomes clearer if a procedure outlined by Lipson and Sheth<sup>(10)</sup> is



applied. The value of  $r$  which must be exceeded in order to certify at a given confidence level that the variations of the two sets of data are interdependent can be obtained from a statistical table (provided in Lipson's text) if the number of variables and number of sets of experimental results are known. For the present case there are 2 variables and 10 pairs of data; for 99% confidence the table gives  $r = 0.765$ . Since all three  $r$  values exceed 0.765 by an appreciable margin, the expected relationship of the two experimental procedures is more than 99% assured for all three time periods of the 150 F method. Further,  $r^2$  represents the fraction of the total variation in one test that is accounted for by the variation in the other; this fraction ranges from 0.79 for the 2-week test to 0.86 for the 6-week test.

#### Time - Total Insolubles Relationships

The 150 F total insolubles versus time data of Table A-3 have been plotted in Figures 3, 4, 5, and 6.

In Figure 3 for the neat fuels, the salient feature is the rapidly increasing curve for fuel D, showing unacceptably high sediment at 4 and 6 weeks. This is strange since the D2274 result for D conforms with the specification for Navy marine diesel fuel (MIL-F-16884), which is 2.5 mg/100 ml maximum total insolubles. The other curves in Figure 3 show variability of about the same magnitude as the small mass values being measured and no trends are evident.

Excluding the curve for  $Amf^2$  for which there is no 2-week data point, curves for the remaining fourteen fuel mixes in Table A-3 are plotted in Figures 4, 5, and 6. When the curves are

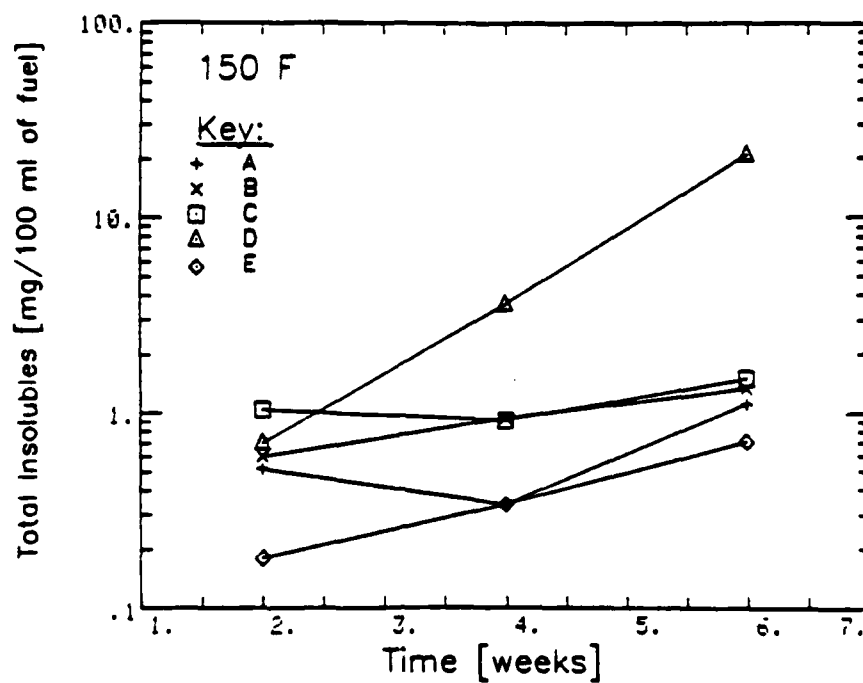


Figure 3 - Nitrogen Reagent Study: Total insolubles versus time for five neat fuels (A,B,C,D,E)

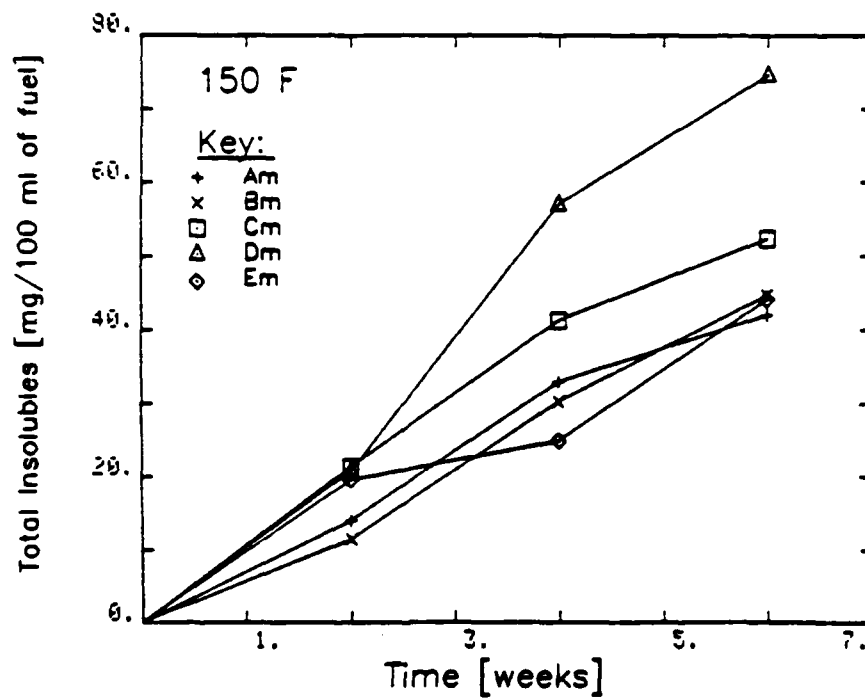


Figure 4 - Nitrogen Reagent Study: Total insolubles versus time for five fuel-reagent mixes (Am,Bm,Cm,Dm,Em; m=5-component nitrogen reagent mixture)

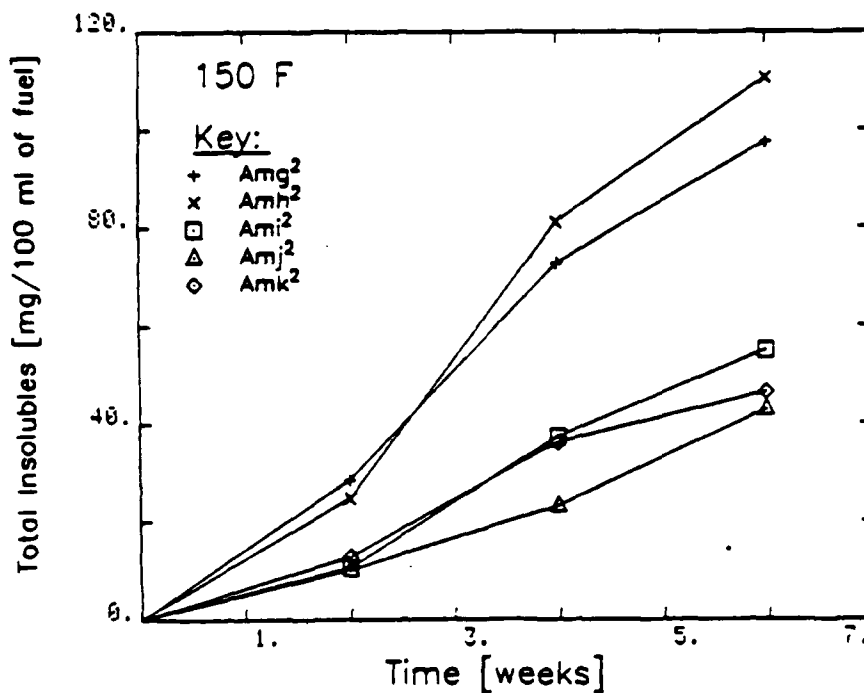


Figure 5 - Nitrogen Reagent Study: Total insolubles versus time for five fuel-reagent mixes ( $\text{Amg}^2$ ,  $\text{Amh}^2$ ,  $\text{Ami}^2$ ,  $\text{Amj}^2$ ,  $\text{Amk}^2$ ;  $g^2$  = reagent g at a concentration of 80 mg nitrogen per liter, etc.)

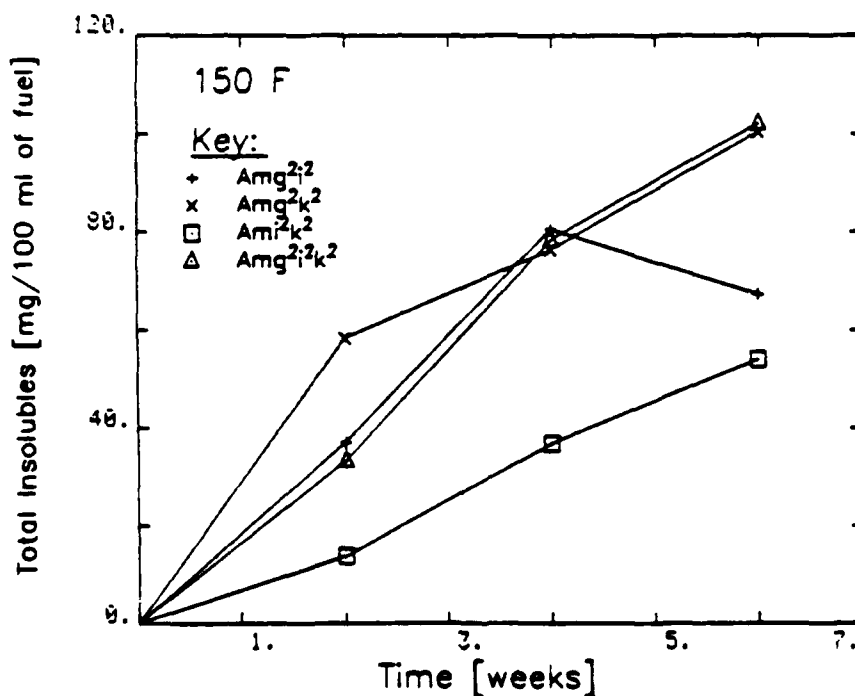


Figure 6 - Nitrogen Reagent Study: Total insolubles versus time for four fuel-reagent mixes ( $\text{Amg}^{2;2}$ ,  $\text{Amg}^{2;k^2}$ ,  $\text{Ami}^{2;k^2}$ ,  $\text{Amg}^{2;2;k^2}$ )

examined for common features, eleven of the fourteen show less deposit produced in the first two weeks than in the second two weeks. The three exceptions are the curves for Cm, Em, and  $Amg^2k^2$ . The smaller production of sediment for the first observation period suggests three possibilities: an autocatalytic reaction in which the product of the reaction catalyzes the formation of additional product, the formation and decomposition of an intermediate compound, or the presence of an inhibiting compound which is slowly destroyed, as by oxidation. If any one of these possibilities is operative, the initial part of the reaction is very slow and is called an induction period. Following this, the reaction rate increases greatly, attains a maximum, and finally slows. In the present instance, one cannot decide just how slow the reaction was at the start, since there are no data except at two weeks. Also, even with more frequent sampling, if there are several concurrent reactions the shape of the observed curve will be a composite. This would more or less mask the shape of the curve of any reaction featuring an induction period. Finally, the precision of the test may not be sufficient to establish the exact shape of the curve. Nevertheless, this type of information plus compositional analysis of the sediment could help immensely toward unraveling the reaction pathway.

## B. Interaction of a Pyrrole and a Thiol

This attempt to determine the effect of a thiol, 1-dodecanethiol (S-1), on sediment production from a diesel-type fuel containing 2,5-dimethylpyrrole (DMP, g) yielded interesting results. Frankenfeld and Taylor<sup>(3)</sup> showed that DMP at a level of 750 mg N/L in No. 2 diesel fuel at 110 F in the presence of 1-dodecanethiol at 3000 mg S/L for 14 days yielded somewhat less total sediment (71.6 mg/100 ml) than without the thiol (85.6 mg/100 ml). However, at longer times there was a reversal of the apparently inhibitory effect of the thiol. The corresponding amounts of total sediment at 28 days were 373.2 and 245.8 mg/100 ml, respectively. Since they reported sediment production by the thiol alone was 0 at 28 days, their result indicated that the thiol has an accelerating effect on the sedimentation reaction in the presence of DMP for the longer storage period.

The current results do not corroborate the Frankenfeld finding of inhibition by 1-dodecanethiol. The data are recorded in Appendix B, Tables B-1 through B-4. The DMP concentration was 750 mg N/L and the maximum ratio of sulfur to nitrogen by mass was 4.00, the same as in the Frankenfeld experiment. Because a shorter maximum storage time (17 versus 28 days) was coupled with a higher storage temperature (150 F versus 110 F), the maximum total insolubles was close to that in the Frankenfeld results (329 versus 373 mg/100 ml). Yet all samples of fuel containing DMP and the thiol produced, on average, more total insolubles than the thiol-free fuel. Thus, at 24 hours, the average total insolubles (in mg/100 ml) was 0.59 for

thiol-free fuel and 1.3, 1.3, 1.3, and 1.1 for S/N mass ratios of 0.25, 0.67, 1.5, and 4.0, respectively. Considering only the thiol-free fuel and S/N mass ratio 4.0 (i.e. DMP at 750 mg N/L and the thiol at 3000 mg S/L, the concentrations in the Frankenfeld study), the total insolubles for each time period are as follows (from Table B-3, values in mg/100 ml):

Aging Time		S/N Mass Ratio	
Days	Hours	0.0	4.0
1	24	0.59	1.1
2	48	5.2	5.7
4	96	20.	30.
8	192	51.	90.
11	264	89.	135.
17	408	134	329

No result here shows less total insolubles for the S/N = 4.0 ratio than for the 0.0 ratio, so there is no evidence of inhibition by the thiol, at least at the S/N = 4.0 ratio. The same is true for the 0.25, 0.67, and 1.50 ratios (Table B-3). The distinctly lower position of the S/N = 0.0 curves in Figure 7 (for filterable insolubles) and in Figure 9 (for total insolubles), compared with the curves for the thiol-containing fuels, makes these relationships quite evident. Figure 8 (for adherent gum versus time) does show the S/N = 0.0 curve lying above the curves for S/N = 0.25 and 0.67 at all observation times longer than 48 hours. However, the amounts of sediment involved are insufficient to bring the S/N = 0.0 curve for total insolubles above the S/N = 0.25 and 0.67 curves in Figure 9. The sediment mass scale in Figure 8 is much magnified; for clarity, the data Tables B-1,2,3 should be consulted.

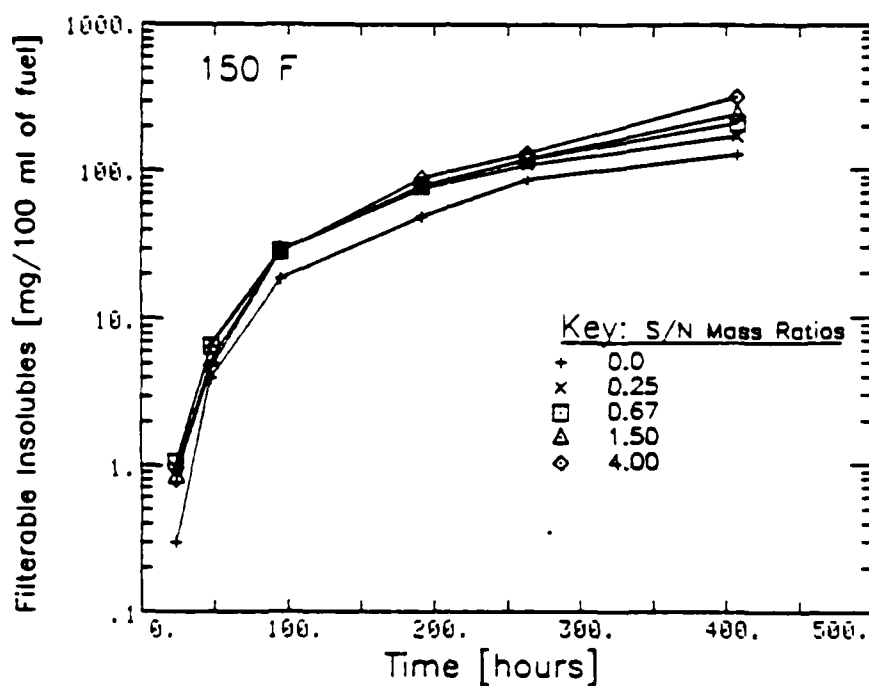


Figure 7 - Interaction of a Pyrrole and a Thiol: Filterable insolubles versus time for five sulfur/nitrogen mass ratios

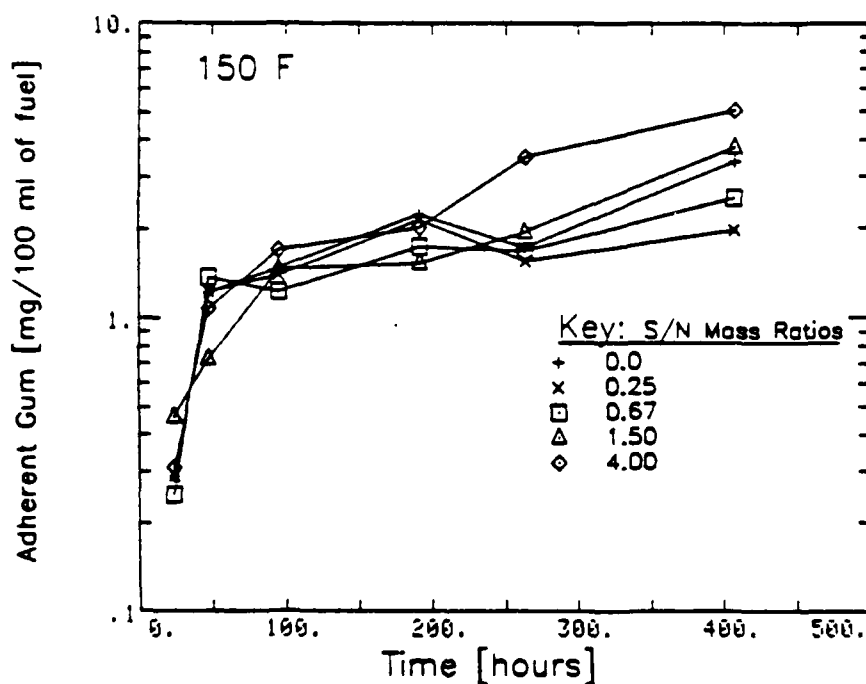


Figure 8 - Interaction of a Pyrrole and a Thiol: Adherent gum versus time for five sulfur/nitrogen mass ratios

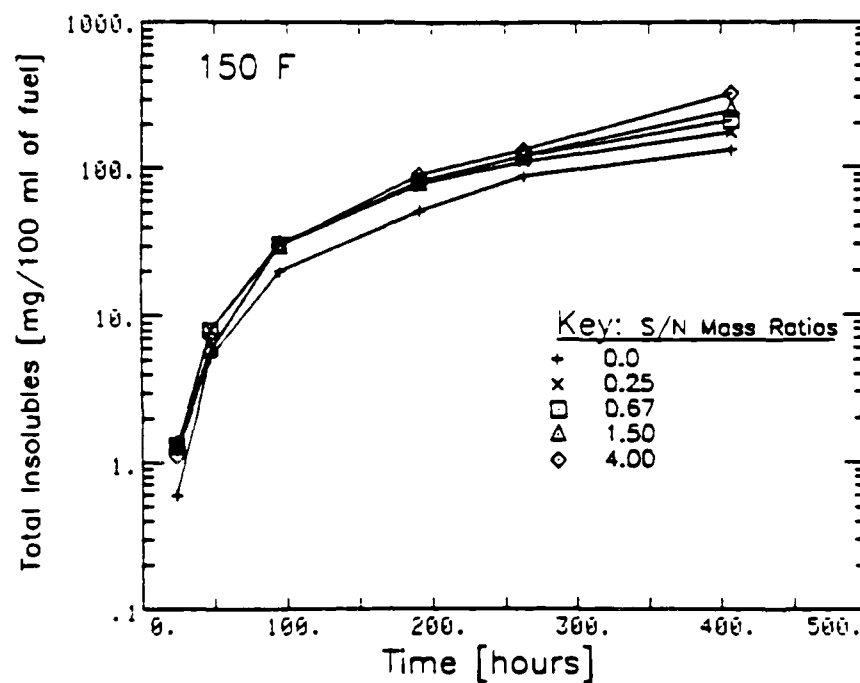


Figure 9 - Interaction of a Pyrrole and a Thiol: Total insolubles versus time for five sulfur/nitrogen mass ratios

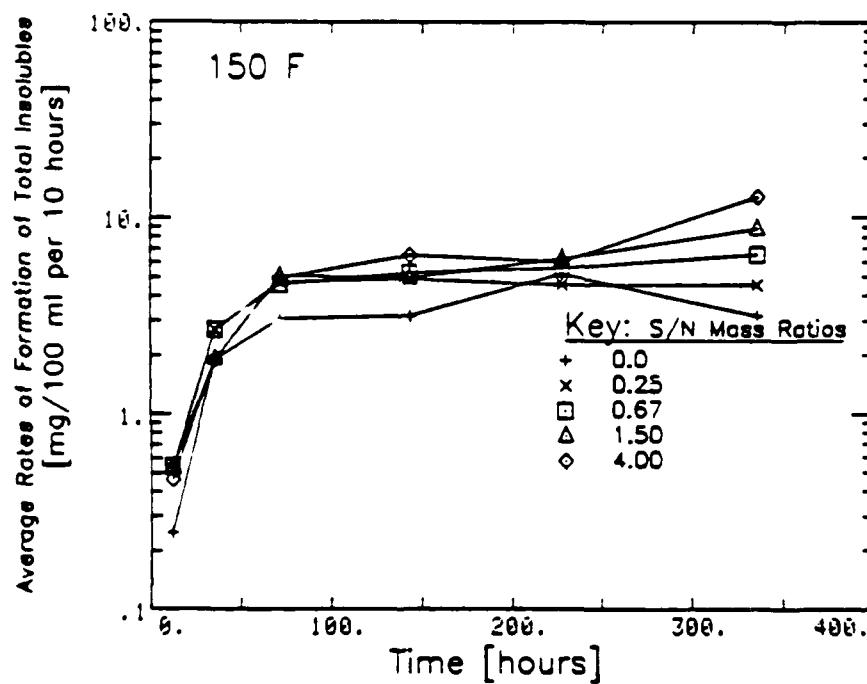


Figure 10 - Interaction of a Pyrrole and a Thiol: Average rates of formation of total insolubles versus time for five sulfur/nitrogen mass ratios



The rate of total insolubles formation (Table B-4 and Figure 10) was a minimum for the thiol-free fuel at almost all observation intervals. Here again there is no evidence of inhibition by the thiol.

The apparently contradictory nature of these results and the Frankenfeld data requires an explanation. One possibility is the use of a higher storage temperature in the current work; if the temperature difference is responsible for a change in the mechanism of sedimentation then short exposure to a higher temperature may not yield the same result as longer exposure to a lower temperature. Also, the results may differ because the base fuels in the two studies were different. At any rate, the current study produced no enlightenment concerning any inhibitory capacity of the thiol, since none was observed.

Regarding the general shapes of the curves: for each S/N mass ratio the amounts of filterable insolubles (Figure 7) and total insolubles (Figure 9) show a smooth increase as storage time increases. This is not true for adherent gum (Figure 8). Here the curves for S/N = 0.0, 0.25, and 0.67 actually show decreases with time at one or two points. Perhaps all of these instances of apparent inversion and other apparent irregularities in the Figure 8 curves may be the result of the values measured being small. The errors of measurement, though not greater than those in Figures 7 and 9 in an absolute sense, are relatively large and cause the curves to crisscross and appear quite irregular. They do sort out after 192 hours, however, and except for the curve for S/N = 0.0 (see above) wind up with the

mass of adherent gum showing successive increases for increasing S/N ratio. Also, the general shape of these curves resembles that for the filterable insolubles, with no evidence of an induction period for either set of curves in the time frame of the experiments (17 days).

An important feature of the curves of sediment mass versus S/N ratio (Figures 11-13) is that all except the 408-hour curves remain essentially horizontal as S/N increases after an initial rise from S/N = 0.0 to S/N = 0.25 (ignoring the expected irregularities in Figure 12 for adherent gum). The average rates of formation of total insolubles, except for the 264-408-hour interval, are independent of S/N ratio (see Table B-4 and Figure 14) as the ratio increases from 0.67 to 4.0. For the 264-408-hour curve the rate jumps from 6.6 to 13 mg/100 ml of fuel per 10 hours. Since the 150 F test often lasts as long as 8 weeks, it would be interesting to know what sort of rate changes would occur in that time frame.

Overall, the presence of thiol has much less effect per unit of concentration at higher concentrations than at lower. At 408 hours aging time, thiol at a concentration of 187.5 mg S/L produces 43 mg/100 ml more total insolubles than the same DMP-containing fuel without the thiol; however, 16 times this concentration of thiol, i.e. 3000 mg S/L, produces 195 mg/100 ml more total insolubles than the DMP-containing fuel without the thiol, only about 4.5 times as much as the lower concentration of thiol. At shorter times the efficiency of additional thiol

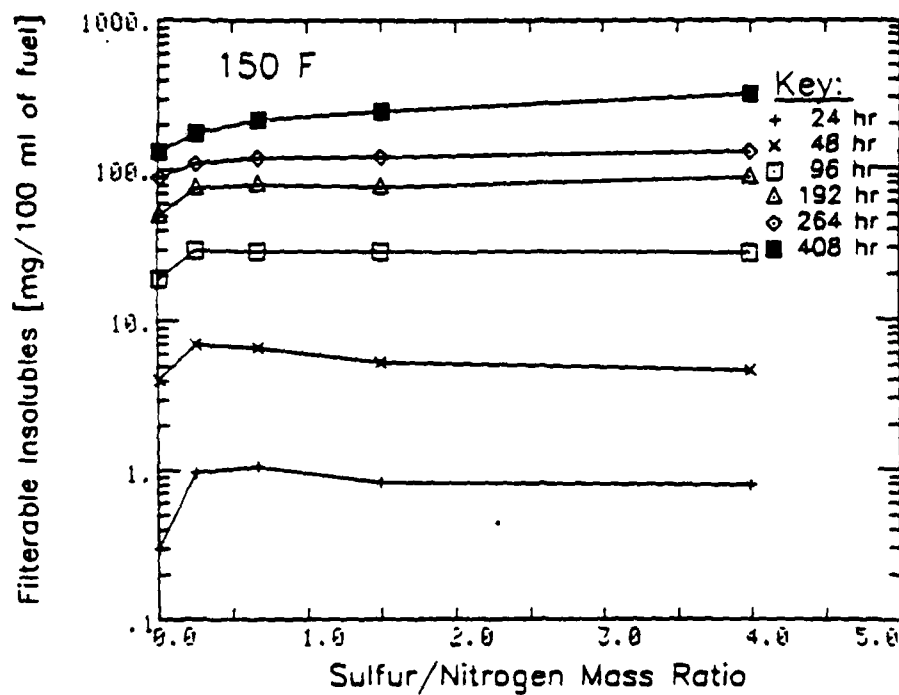


Figure 11 - Interaction of a Pyrrole and a Thiol: Filterable insolubles versus sulfur:nitrogen mass ratio for six time periods

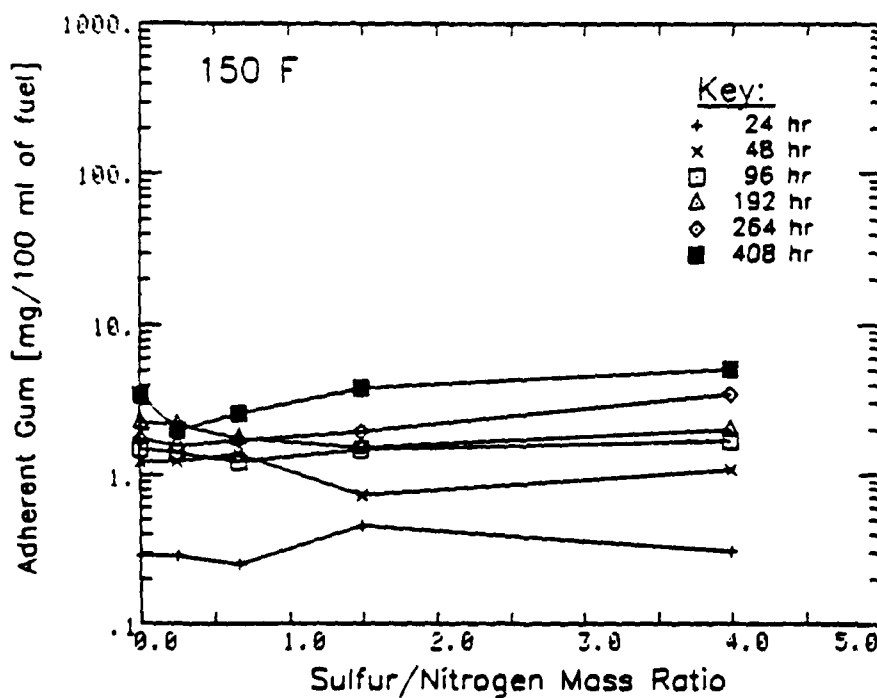


Figure 12 - Interaction of a Pyrrole and a Thiol: Adherent gum versus sulfur:nitrogen mass ratio for six time periods

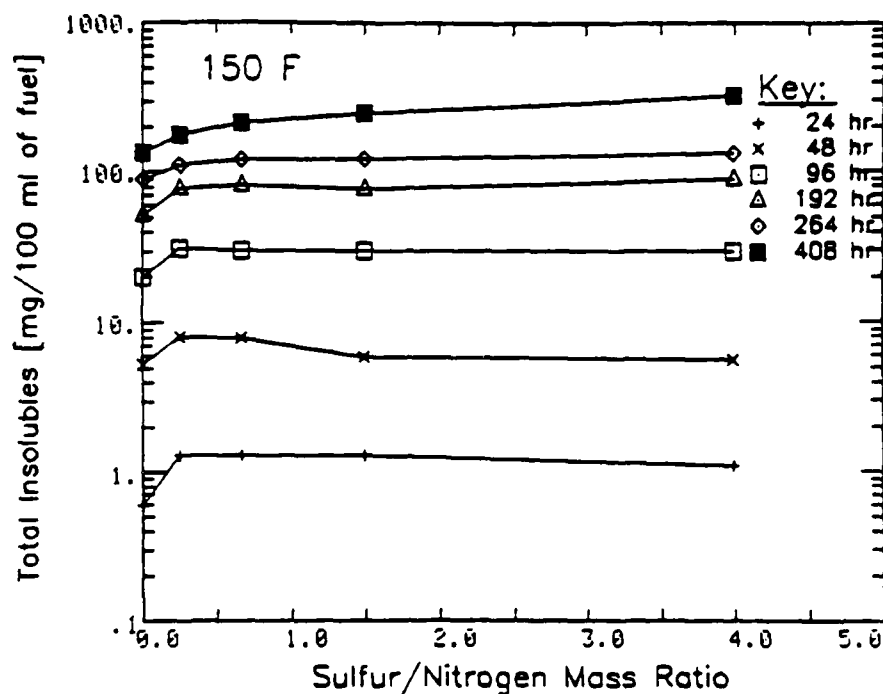


Figure 13 - Interaction of a Pyrrole and a Thiol: Total insolubles versus sulfur:nitrogen mass ratio for six time periods.

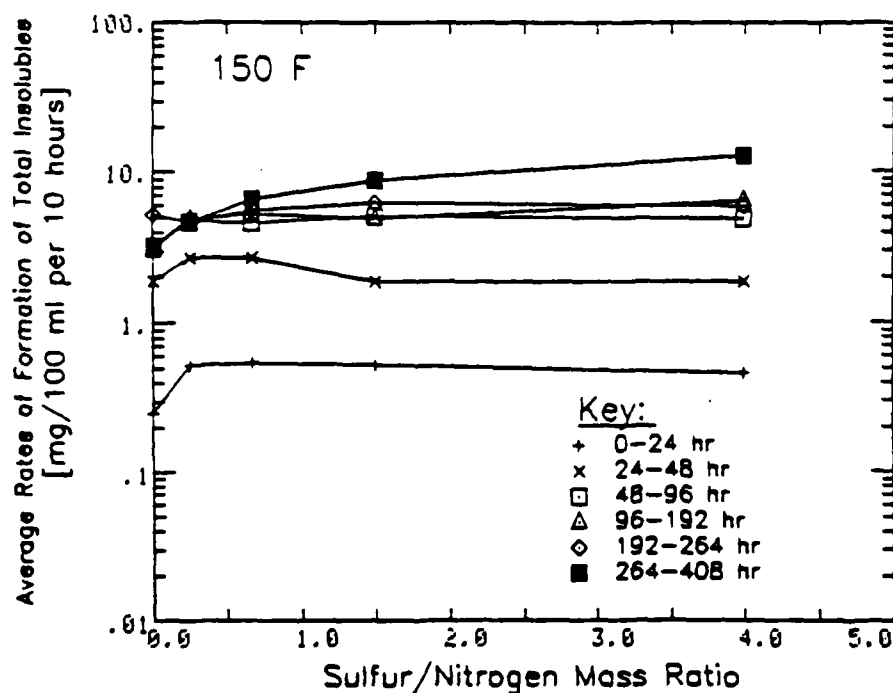


Figure 14 - Interaction of a Pyrrole and a Thiol: Average rates of formation of total insolubles versus sulfur:nitrogen mass ratio for six time intervals

is much less; at 48 hours the results show a little less total insolubles at S/N = 1.5 and 4.0 than at 0.25 and 0.67 (though more than at 0.0, so this is not a case of inhibition).

The data considered as a whole suggest that a small amount of the thiol may interact with DMP or other fuel components and produce extra sediment, but additional thiol may not be able to find available reactive molecules or may not be able to react with those it does contact because of an unfavorable entropy factor. That is, the system quickly may be saturated with thiol and additional thiol may remain in solution in a relatively inert status. At longer storage times (or at higher temperatures, or both) some of this extra thiol may be activated and produce sediment.

Data from Table B-3 may be used to calculate the efficiency of different concentrations of added 1-dodecanethiol as a sedimentation agent in the presence of DMP. The following data apply to storage for 408 hours of base fuel containing DMP at 750 mg N/L:

1. S/N mass ratio...	0.0	0.25	0.67	1.5	4.0
2. Concentration of 1-dodecanethiol, mg S/L.....	0.0	187.5	500.	1125.	3000.
3. Total insolubles, mg/100 ml.....	134.	177.	216.	251.	329.
4. Net total insolubles produced by the thiol, mg/100 ml.....	--	43.	82.	117.	195.
5. Efficiency, (#4/#2) X 10..	2.3	1.6	1.0	0.65	

The "efficiency" values are the number of mg total insolubles produced by one mg sulfur (as the thiol) in fuel containing DMP at 750 mg N/L. At  $S/N = 0.25$  the thiol efficiency is actually greater than that of the DMP itself. In the fuels here the DMP produces  $(134 \times 10)/750$  or 1.8 mg total insolubles per one mg nitrogen. At  $S/N = 0.25$  (187.5 mg S/L) the thiol efficiency of 2.3 is thus 28% greater than that of DMP. However, at  $S/N = 4.0$  (3000 mg S/L) the thiol efficiency is only 0.65, 64% less than that of DMP.

### C. Interaction of a Pyrrole and a Piperazine

Two nitrogen reagents, 2,5-dimethylpyrrole (DMP, reagent g) and 2-methylpiperazine (reagent j), were used in this study. In all of the four test methods employed here the experiments were designed to yield data in 2 X 2 factorial form. Mathematical analysis of the data was believed to be statistically rigorous for three of the methods, and conclusions based on this analysis should be meaningful. Although the data for the ASTM D3241 (JFTOT) test were also in the 2 X 2 format, the statistical treatment used in the other tests was not applied because the JFTOT data are not presumed to be additive.

#### D3241 (JFTOT) Test

The data (Appendix, Table C-1) were obtained using a test section temperature of 260 C (500 F). A relatively moderate concentration of 2-methylpiperazine, 100 mg N/L, results in very poor fuel performance: the  $\Delta P$  value reaches 125 mm in an average of about 40 minutes and the spun TDR is about 24. The MIL-T-5624 specification for JP-5 limits  $\Delta P$  to 25 mm for the 150-minute duration of the test using a 260 C test section temperature. In the absence of a spun TDR specification for JP-5, several groups<sup>(11,12)</sup> have adopted 13 (maximum) as a pass value. Surprisingly, the same nitrogen concentration in the form of DMP shows a very low average for  $\Delta P$  (2 mm) at 150 minutes; however, the spun TDR is about 25.

The diesel-type fuel containing 100 mg N/L in the form of 2-methylpiperazine fails to meet the JP-5 norms but the same fuel containing the same nitrogen concentration in the form of

DMP passes the  $\Delta P$  test but fails the spun TDR test. The Nitrogen Reagent Study showed that 2-methylpiperazine at 120 mg N/L in the presence of DMP at 40 mg N/L and six other nitrogen reagents at 200 mg N/L (total) required 42 minutes for  $\Delta P$  to reach 125 mm; on the other hand, DMP at 120 mg N/L plus 2-methylpiperazine at 40 mg N/L and the same six other nitrogen reagents at 200 mg N/L (total) required only 28 minutes for  $\Delta P$  to reach 125 mm (see Table A-1). The base fuel was the same as that used in the current study. Under JFTOT conditions, then, 2-methylpiperazine in the presence of certain other nitrogen reagents yields a somewhat more stable fuel than DMP in the presence of those other reagents, but with no other reagents present the fuel plus DMP is more stable than the fuel plus 2-methylpiperazine. The individual behavior of the nitrogen reagents is apparently a function not only of the nature and concentration of the particular reagent but also of the nature and concentration of other reagents which may be present.

The current JFTOT results for the case when both DMP and 2-methylpiperazine are present show that the system requires, on average, somewhat longer times for  $\Delta P$  to reach the 125 mm level than when the piperazine is present alone. Since DMP alone produces only very small  $\Delta P$  values, the data suggest that DMP may actually have inhibitory effect on fuels containing the piperazine.

Comparison of the JFTOT results with those from other tests shows that 2-methylpiperazine is a much worse actor under JFTOT conditions, i.e. short exposure at high temperatures (above



250 C), than under much longer exposure at lower temperatures (150 C and below). In fact, 2-methylpiperazine has well-established inhibitory characteristics at lower temperatures in fuels containing DMP.

#### D2274 Test

The nitrogen reagent 2-methylpiperazine at the 375 mg N/L level in base fuel yields lower total insolubles than the base fuel alone (0.21 vice 0.71 mg/100 ml). The same concentration of the piperazine in base fuel containing DMP at 375 mg N/L yields total insolubles of 1.77 mg/100 ml, less than a third of that when only the DMP is present (5.67 mg/100 ml). These data are averages of the triplicate data recorded in Table C-2. Since the diesel fuel specification MIL-F-16884G requires that total insolubles by ASTM D2274 not exceed 2.5 mg/100 ml of fuel, the addition of the piperazine brings the fuel containing DMP within the specification.

For the D2274 test (and the 150 C and 150 F tests also) the "factorial design" of the experiments should be explained. Factorial design improves on classical design by enabling the experimenter not only to estimate the individual effects of each of several factors (the independent variables) on the value of a dependent variable, but also to estimate the experimental error in the test data, the effect of interactions of the factors with each other, and the confidence levels attached to all these effects. A "2 X 2 factorial" is an experiment involving two factors operating at two levels each. In the present instance the factors are the reagents DMP and 2-methylpiperazine and the

levels are concentrations (one of which is zero here).

An analysis of variance is particularly useful in factorial experiments where several independent sources of variation may be involved. The analysis is based upon the fact that the variance of the observations is the sum of the variances of the independent sources. The total variation can therefore be ascribed to the main factors (the presence or absence of DMP and 2-methylpiperazine), interacting factors, and a residual (experimental) error. The significance of each main factor and of the interaction factor, relative to the experimental error can then be tested using the F-statistic for the level desired. The mechanics of the calculation may be found in texts on experimental design, e.g. that of Lipson and Sheth<sup>(13)</sup>.

The mean square ratios (MSR), the ratios of the mean square for the two main factors and for their interaction to the mean square of the residual error, are shown in Table 9. For example, the MSR of the DMP concentration factor in the yield of filterable insolubles is shown as 338. This individual MSR value has been compared with the F-statistics for the 95% ( $F_{0.05}$  value) and 99% ( $F_{0.01}$  value) confidence levels to determine the relative significance of the effect of the factor on the value of the dependent variable, the amount of filterable insolubles in unit volume of fuel. The result is "HS+". The term "confidence level" refers to the probability that the effect measured is real and not the result of experimental error. In the current study, a rather conservative evaluation of these data is employed. If  $MSR > F_{0.01}$ , the measured effect is considered high-

ly significant (HS); for  $F_{0.01} > \text{MSR} > F_{0.05}$ , probably significant (PS); for  $F_{0.05} > \text{MSR}$ , not significant (NS). Signs attached to the significance levels indicate whether the effect measured increases (+) or decreases (-) the value of the dependent variable. A result of "HS+" would mean that there is better than a 99% chance that the factor level causes an increase in the dependent variable; "PS-" means that the factor has a 95 to 99% chance of producing a decrease in the dependent variable. Even "NS-" can often mean that the measured decrease results from the factor level more than nine times out of ten -- comparison of the MSR value with the  $F_{0.10}$  statistic would be required to be sure.

The results of the statistical calculations for the 2 X 2 factorial data of Table C-2 are summarized in Table 9.

TABLE 9  
MEAN SQUARE RATIOS IN D2274 TEST  
Interaction of a Pyrrole and a Piperazine

$$F_{0.05} = 5.32; F_{0.01} = 11.3$$

Signif- icance	<u>Filterable Insolubles</u>			<u>Adherent Gum</u>			<u>Total Insolubles</u>		
	DMP <sup>a</sup>	MPPZ <sup>b</sup>	DMP + MPPZ	DMP	MPPZ	DMP + MPPZ	DMP	MPPZ	DMP + MPPZ
	338	108	104	10	25	0.12	287	123	70
	HS+	HS-	HS-	PS+	HS-	NS-	HS+	HS-	HS-

<sup>a</sup>DMP = 2,5-dimethylpyrrole at 375 mg N/L

<sup>b</sup>MPPZ = 2-methylpiperazine at 375 mg N/L

The negative effect of the piperazine on sedimentation is evident upon inspection of Table C-2; the values for filterable

insolubles, adherent gum, and total insolubles for the mixture of DMP and the piperazine are all less than the corresponding values for DMP alone. The assurance that this judgment is correct is clear from the fact that all the mean square ratio values greatly exceed the 11.3 F-statistic for the 99% confidence level. For DMP two of the three values exceed 11.3, but the value for adherent gum (10) falls between 5.32 and 11.3, so the positive effect of DMP on adherent gum formation falls between the 95% and 99% confidence levels and is rated "probably significant".

The interaction of the piperazine with DMP is the most interesting feature of Table 9. The mean square ratios for the "DMP + MPPZ" combination are large enough for the interaction to be rated "highly significant" for filterable insolubles and for total insolubles. While the effect is negative for adherent gum, the mean square ratio is small and the decrease produced is considered "not significant". The reason for the small ratio is the relatively large variations for the adherent gum data, in particular for the fuel containing only DMP. Also, since the gum effect is not significant, the decrease in filterable insolubles must be the major factor in the stabilizing influence of the piperazine.

#### 150 C Test

In the 150 C test procedure the concentrations of DMP and 2-methylpiperazine (each at the 375 mg N/L level) were the same as were used for the D2274 test.

The reference blotter ratings and the reflection meter readings are reported in Table C-3. The strong destabilizing effect

of DMP is apparent in the high reference blotter ratings for the fuel containing only DMP; the low reflection meter readings corroborate this. Also, the inhibitory characteristics of the 2-methylpiperazine are clearly seen. Alone, this nitrogen reagent yields blotter ratings about the same as for the neat base fuel. In fuel containing DMP addition of this reagent reduces the mean reference blotter rating from 17 to 4. It also effects an increase in the mean reflection meter reading from about 24 to about 55 (the greater the reflectance, of course, the smaller the deposit density). Since reflectance readings are not additive, the statistical analysis of the 2 X 2 factorial data is reported here only for the reference blotter ratings:

Mean Square Ratios

DMP	2-Methylpiperazine	DMP + 2-Methylpiperazine
2138, HS+	1077, HS-	1061, HS-

$$F_{0.05} = 4.35; F_{0.01} = 8.10$$

Estimation of the precision of these two types of evaluation (reference blotter versus reflection meter) is possible using the standard deviations of the values recorded. The table which follows presents the means, standard deviations, and the standard deviations as a percentage of the mean for both reference blotter and reflection meter results:

### Reference Blotter Ratings

DMP						
	Absent			Present		
	Mean	$\sigma$	%*	Mean	$\sigma$	%*
Absent	1.39	0.61	43.9	17.3	0.77	4.44
MPPZ**						
Present	1.33	0.49	36.8	4.11	1.41	34.3

### Reflection Meter Readings

DMP						
	Absent			Present		
	Mean	$\sigma$	%*	Mean	$\sigma$	%*
Absent	72.5	2.05	2.83	24.4	4.16	17.1
MPPZ**						
Present	72.2	1.07	1.48	55.0	1.43	2.60

\*% = 100  $\sigma$ /Mean

\*\*MPPZ = 2-methylpiperazine

The results of the comparison clearly favor the reflection meter readings, but their greater precision may be simply the result of the values measured being larger. Also, interpretation of the reflection meter readings is difficult because the meter values cannot be directly translated into deposit masses. On the other hand, the relationship of blotter density to deposit mass is straightforward.

### 150 F Test

Table C-4 (Appendix) lists the 150 F triplicate data for time periods of 3 days, 1 week, 2 weeks, 4 weeks, and 8 weeks. The nitrogen concentration was 375 mg/L for the DMP and for the 2-methylpiperazine (750 mg N/L when both compounds were present).

As in the D2274 and 150 C tests, the fuel containing DMP

produced the greatest amounts of insolubles and gums. Also, 2-methylpiperazine plus fuel behaved very much like the fuel alone. For 14 days the inhibitory capacity for the piperazine, noted in the D2274 and 150 C tests, was again quite evident in that the fuel containing both nitrogen reagents produced little more sediment than the neat fuel. After two weeks, however, the amount of total insolubles jumped considerably, though the figures remained well below those for the fuel plus DMP (see Figures 15 and 17, in particular the 4- and 8-week data points).

The results are quite different for adherent gum (see Table C-4 and Figure 16). At 1, 4, and 8 weeks the values (in mg/100 ml) for DMP plus the piperazine are 1.89, 3.03, and 2.83, respectively, each value greater than the corresponding one for DMP alone: 0.43, 1.38, and 1.02. The mean square ratios presented in Table 10 show a highly significant positive deviation due to the piperazine at 1 week and a probably significant positive deviation at 4 weeks; increases at 2 and 8 weeks are smaller and considered not significant. The presence of the piperazine thus tends to enhance the formation of adherent gum even though the overall effect of the piperazine is to reduce sedimentation, as is evident from the unbroken array of highly significant mean square ratios of the negative type under the MPPZ (2-methylpiperazine) and D + M (i.e. DMP + MPPZ) columns for total insolubles.

High temperatures (JFTOT results) and long times (such as 8 weeks at 150 F) apparently tend to overcome the inhibitory effect of 2-methylpiperazine. Although the 150 F results still show a "highly significant" negative interaction at 8 weeks, the

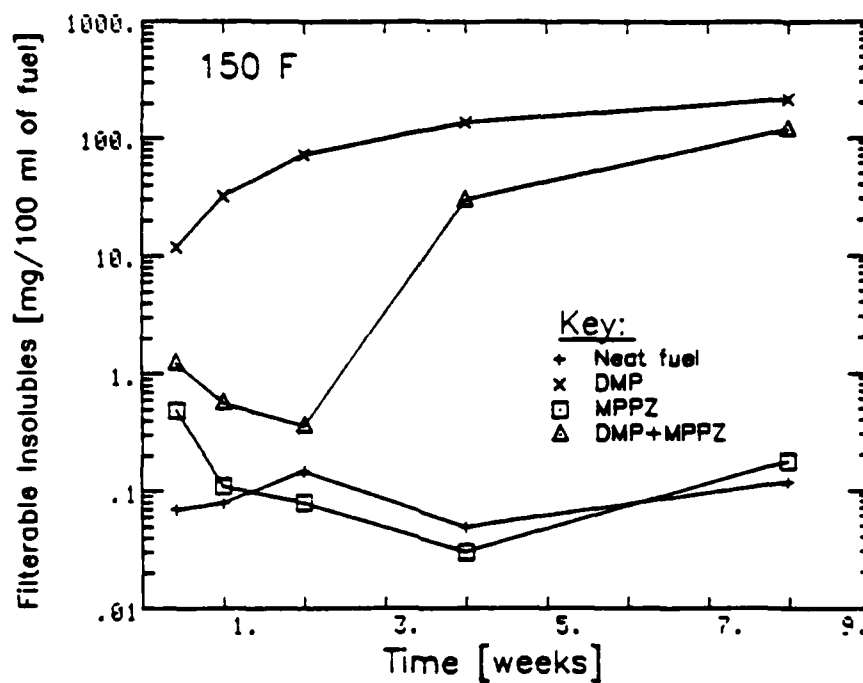


Figure 15 - Interaction of a Pyrrole and a Piperazine: Filterable insolubles versus time for neat fuel, for 2,5 dimethylpyrrole (DMP), for 2-methylpiperazine (MPPZ), and for DMP + MPPZ

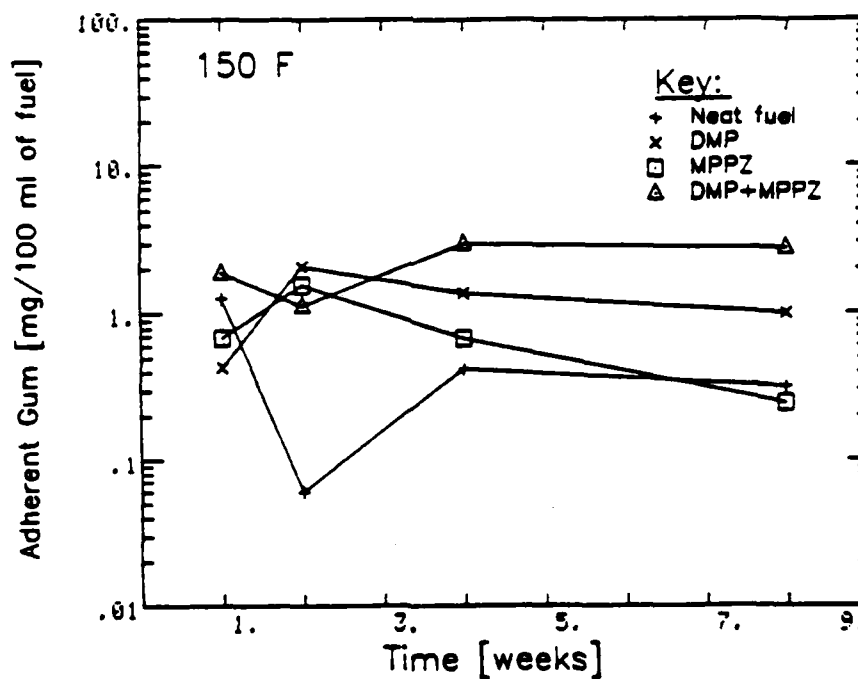


Figure 16 - Interaction of a Pyrrole and a Piperazine: Adherent gum versus time for neat fuel, for 2,5 dimethylpyrrole (DMP), for 2-methylpiperazine (MPPZ), and for DMP + MPPZ



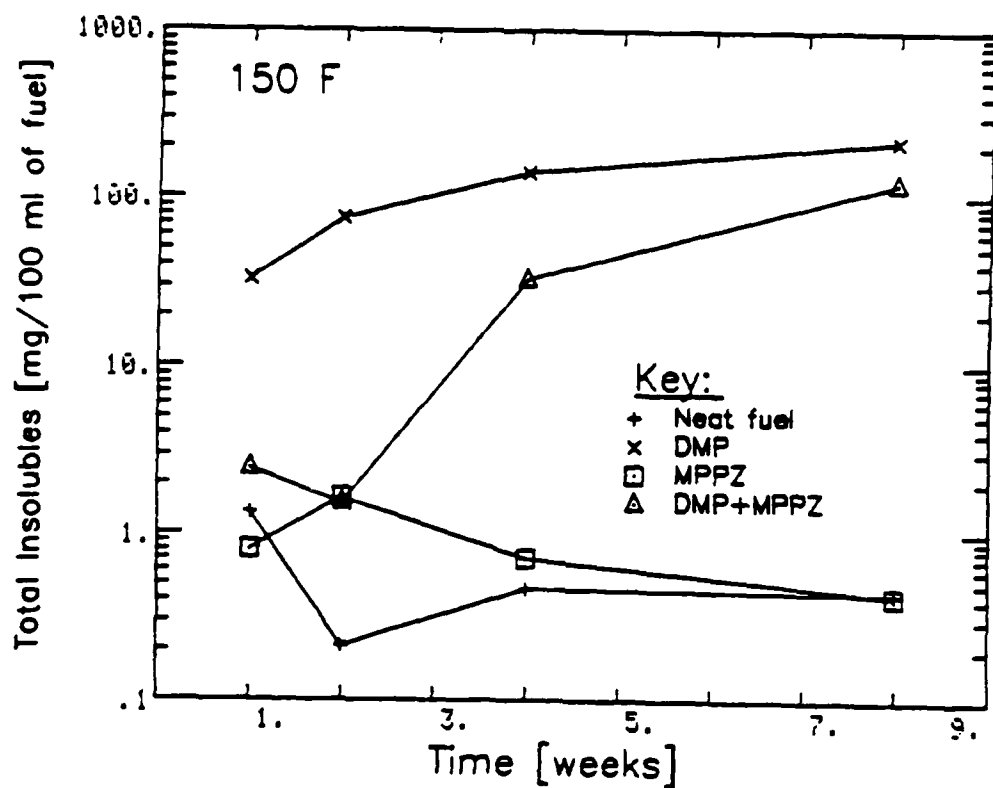


Figure 17 - Interaction of a Pyrrole and a Piperazine: Total insolubles versus time for neat fuel, for 2,5 dimethylpyrrole (DMP), for 2-methylpiperazine (MPPZ), and for DMP + MPPZ

TABLE 10

## MEAN SQUARE RATIOS IN 150 F TEST

Interaction of a Pyrrole and a Piperazine

$$F_{0.05} = 5.32; F_{0.01} = 11.3$$

Storage Time	Filterable Insolubles		Adherent Gum		Total Insolubles		
	DMP <sup>a</sup>	MPPZ <sup>b</sup>	D + M <sup>c</sup>	DMP	MPPZ	D + M	D + M
3 days	1215 HS+	813 HS-	951 HS-	134 <sup>d</sup> HS+	8.55 <sup>d</sup> PS-	60.5 <sup>d</sup> HS-	828 HS+ 390 HS- 577 HS-
1 week	692 HS+	652 HS-	654 HS-	7.13 PS+	44.9 HS+	236 HS+	615 HS+ 535 HS- 499 HS-
2 weeks	487 HS+	481 HS-	480 HS-	6.52 PS+	0.75 NS+	15.7 HS-	396 HS+ 369 HS- 399 HS-
4 weeks	1125 HS+	470 HS-	469 HS-	27.9 HS+	9.19 PS+	4.77 NS+	1430 HS+ 554 HS- 559 HS-
8 weeks	249 HS+	21.3 HS-	21.3 HS-	8.93 PS+	2.50 NS+	2.94 NS+	232 HS+ 18.7 HS- 18.7 HS-

<sup>a</sup>DMP = 2,5-dimethylpyrrole at 375 mg N/L<sup>b</sup>MPPZ = 2-methylpiperazine at 375 mg N/L<sup>c</sup>D + M = DMP + MPPZ, each at 375 mg N/L<sup>d</sup>A solvent problem in the analysis makes these results questionable; the values for total insolubles at 3 days are also uncertain to some extent since they include the adherent gum.

curves in Figures 15 and 17 indicate that the filterable insolubles and total insolubles for the DMP plus 2-methylpiperazine combination is approaching that for DMP alone. Such chemical changes as oxidative or thermal degradation of the piperazine or its possible coupling with other species in the fuel may effectively cancel its protective function. What is not known is whether such results at 150 F or above can be extrapolated to lower temperatures. Possibly the inhibitory quality of 2-methylpiperazine could be indefinitely maintained at ambient temperatures.

The curves of Figures 15, 16, and 17 do not reveal the orders or the mechanisms of the sedimentation reactions. Figure 15 could indicate similar curve form for the DMP and DMP + MPPZ curves since the early irregularity of the DMP + MPPZ curve may be the result of experimental error. The shapes of both curves could then apply to single first-order reactions going toward completion. Either or both curves, on the other hand, could be concealing an induction period which, if true, would require at least two reactions. The discussion of the results of the Nitrogen Reagent Study considered the latter possibility since eleven of fifteen curves there seemed to have at least the rudiments of the proper form. The relationship of curve form to reagents added has not been fully studied. In the study of reaction mechanisms related to such curve forms the importance of identifying the compounds responsible for instability, along with the products they form, is a basic requirement for success. A good start in this direction has been made by Frankenfeld and Tay-

lor<sup>(3)</sup>. Their report identified critical functional groups in compounds involved in the sedimentation process and discussed some of their possible end products.

#### D. Concentration Effects of a Pyrrole

This series of experiments measures sediment formation as a function of the concentration of the nitrogen reagent 2,5-dimethylpyrrole (DMP).

The partial data collected to this time (early 1983) from the D3241 (JFTOT) test (see Table D-1 in the Appendix) have been insufficient to establish clear relationships except that higher concentrations of DMP produce unacceptably high deposits. In the JFTOT procedure, pressure drop across the test filter measures the tendency of the fuel to form particulates (or filterable insolubles) which might clog fuel orifices or filters, whereas deposits on the heated test section surface measure the tendency of the fuel to form gum or varnish on heat exchanger tubes or on other heated surfaces. To pass the JFTOT test, a jet fuel meeting JP-5 (MIL-T-5624) specifications must have  $\Delta P_{\max} = 25$  mm and a visual deposit rating below 3. The JFTOT result for the base fuel in the current studies show  $\Delta P = 0$  mm and the visual deposit rating = 0 (spun TDR = 2.3). Although there is no spun TDR specification for JP-5, the pass value of 13 is used by Exxon Research and Engineering<sup>(12)</sup>.

The JFTOT results for a DMP concentration of 93.75 mg N/L are mixed. The pressure drop ( $\Delta P$ ) is low, 1.7 mm, but the visual deposit rating is 2 and the spun TDR is 25. The JFTOT conditions (high temperature, short exposure time) thus produce high gums (adherent deposits) but not much filterable sediment in DMP concentrations of 93.75 to 375 mg N/L.

The D2274 tests which have been completed (Table D-2) are

more informative. Increasing DMP concentration produces increases in both adherent gum and filterable insolubles which are approximately linear over the whole concentration range. The low-concentration filterable insolubles values and the adherent gum data do show some departure from linearity, but Figures 18 and 19 show that the case for linearity is reasonable for both types of sediment. The sagging values in Figure 18 could be the result of a relatively greater loss of fines through the filter in the low-concentration samples. The irregular values in Figure 19 would hardly be irregular at all if the scale were the same as in Figure 18. The straight lines in both figures are not least-square curves but were drawn through the origin and split the data. Drawing the curves in this fashion suggests, but hardly proves, proportionality of concentration and sediment.

Figure 20, the curve for total insolubles versus DMP concentration, is nearly identical with Figure 18 since the added adherent gum values are relatively small.

Frankenfeld and Taylor<sup>(3)</sup> state that sediment formation seems to be first order in DMP. The data reported here do not permit an in-depth kinetic analysis, but near-proportionality of sediment mass and concentration of DMP does tend to confirm the Frankenfeld conclusion.

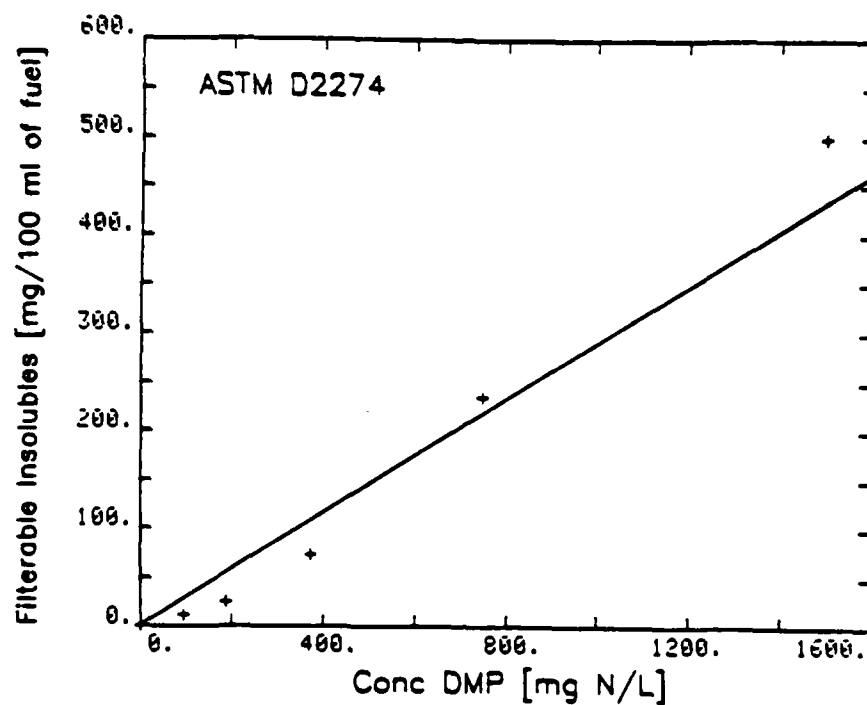


Figure 18 - Concentration Effects of a Pyrrole: Filterable insolubles versus concentration of 2,5 dimethylpyrrole (DMP)

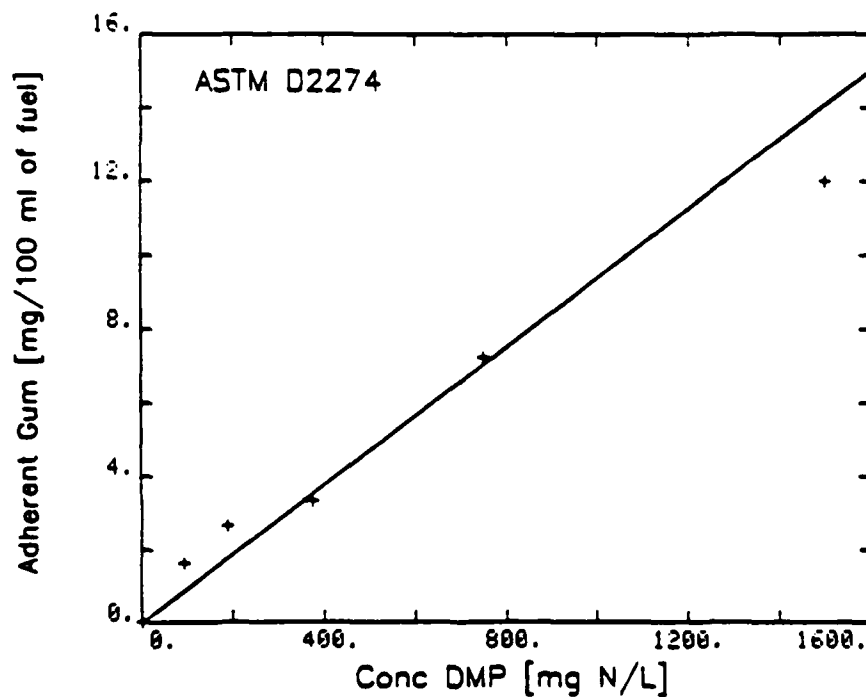


Figure 19 - Concentration Effects of a Pyrrole: Adherent gum versus concentration of 2,5 dimethylpyrrole (DMP)

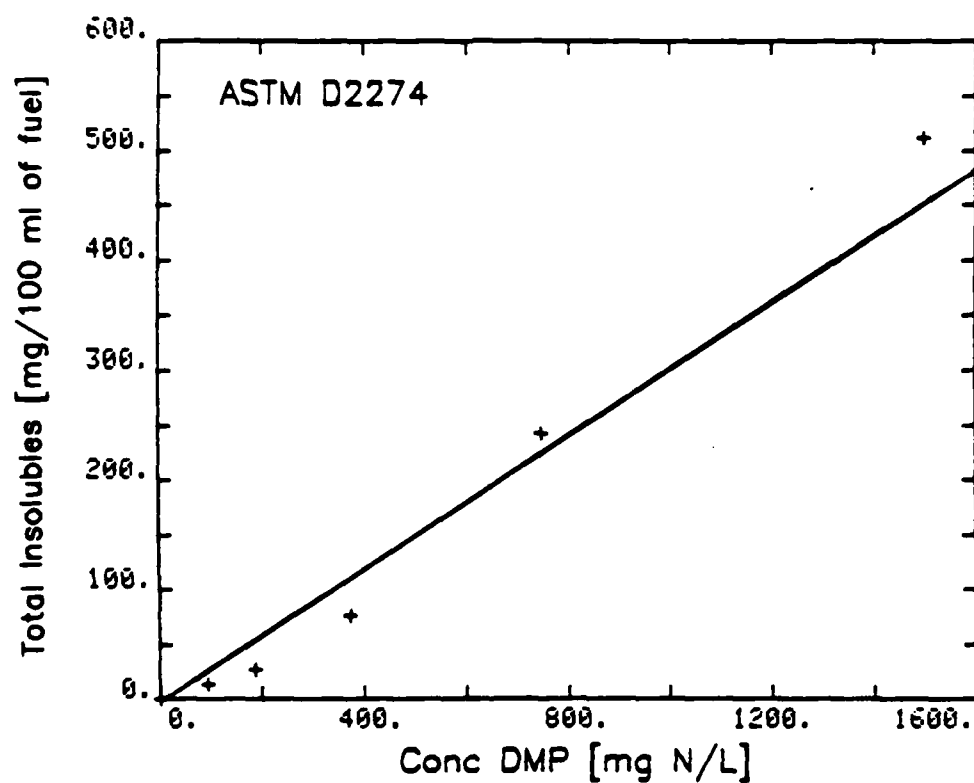


Figure 20 - Concentration Effects of a Pyrrole: Total insolubles versus concentration of 2,5 dimethylpyrrole (DMP)



## E. Screening of Nitrogen, Oxygen, and Sulfur Reagents

The initial data for this study are recorded in Tables E-1 and E-2 of the Appendix. They are of interest in establishing the nature and degree of interaction of various compounds with the base fuel. However, the data available are from the D3241 (JFTOT) and D2274 tests only and there are no data testing the interaction of the compounds with DMP. The compounds are from classes known to be involved, directly or indirectly, in the sedimentation process, as reactants, promoters, inhibitors, catalysts, etc. The specific activity of the compounds chosen is unknown and forms the basis of this investigation. Five are nitrogen compounds; one is a sulfur compound and one is an oxygen compound.

The JFTOT data pertain to the neat base fuel (also reported in Table D-1) and to the 375-mg-N/L concentration for 2-methylpiperazine (code j in the tables). The current data provide a concentration comparison with the 100-mg-N/L level of 2-methylpiperazine reported in Table C-1. Thus:

Concentration of 2-metnylpiperazine	Time (min) for $\Delta P$ to reach 125 mm	Time (min) for $\Delta P$ to reach 250 mm	Spun TDR	Source Table
100 mg N/L	43	49	17	C-1
	35	47	30	C-1
375 mg N/L	17	22	48	E-1

There are no surprises here -- the clogging of the test filter occurs in less than half the time and the spun TDR is about

twice as large when the 2-methylpiperazine concentration is quadrupled. As noted in connection with the study "Interaction of a Pyrrole and a Piperazine", at JFTCT conditions 2-methylpiperazine has a decidedly positive effect on sedimentation.

Among the seven reagents tested by D2274 only DMP and 1,2,5-trimethylpyrrole gave substantial deposits. The reagents 2-methylindole, 2-methylpiperazine, isoquinoline, 2,6-di-tert-butylphenol, and 1-dodecanethiol all yielded total insolubles of less than 1.2 mg/100 ml. The Navy marine diesel fuel specification (MIL-F-16084G) is 2.5 mg/100 ml (maximum). The concentrations used in the tests reported in Table E-2 were as follows: nitrogen, 375 mg/L; sulfur, 428 and 858 mg/L; and oxygen, 858 mg/L. The results suggest that, at these levels, none of these compounds when present alone would cause sedimentation problems. The study "Interaction of a Pyrrole and a Thiol" showed that 1-dodecanethiol has a positive interaction with DMP and the pyrrole-piperazine study showed that 2-methylpiperazine interacts negatively with DMP. It is not known at this point how 2-methylindole, isoquinoline, 1,2,5-trimethylpyrrole, and 2,6-di-tert-butylphenol would react in the presence of DMP.

## SUMMARY OF FINDINGS AND CONCLUSIONS

1. The nature of the base fuel is important in determining the effects of certain nitrogen-containing reagents on the stability of fuels.
2. The compounds 2,5-dimethylpyrrole (DMP) and 1,2,5-trimethylpyrrole (TMP), when added to a stable diesel-type fuel, produced more total insolubles than any of the other reagents tested. In the ASTM D2274 test DMP at the 750-mg-nitrogen-per-liter level yielded up to 2500 times as much total insolubles as the base fuel; TMP at the same level yielded about 560 times as much.
3. Up to a level of 1500 mg of nitrogen per liter, additions of DMP to a stable diesel fuel produced a mass of total insolubles which was approximately proportional to the DMP concentration (D2274 test).
4. Four different stability test methods ranked the fuels and fuel-reagent mixes with reasonable consistency. The results of ASTM D2274 deviated the least from the overall rankings based on ASTM D3241, the 150 C test, ASTM D2274, and the 150 F test. The high-temperature, short duration ASTM D3241 test deviated the most.
5. The sulfur-containing reagent 1-dodecanethiol interacted with DMP at 150 F to produce more total insolubles than the sum total insolubles produced by the thiol and the DMP separately.
6. The sulfur-nitrogen mass ratio (S/N) in the thiol-DMP-fuel mixes was not critical. In storage at 150 F through 96 hours, increasing S/N from 0.25 to 4.00 produced no more total insolu-

bles than were produced by the 0.25 ratio (750-mg-nitrogen-per-liter level for DMP). Increases of S/N above 0.25 produced increases in total insolubles which were less than proportional to the S/N value in storage for 192, 264, and 408 hours.

7. No sedimentation-inhibiting effect of 1-dodecanethiol was observed at 150 F for any S/N mass ratio from 0.25 to 4.00 in fuel containing DMP at a concentration of 750 mg nitrogen per liter. This finding contrasts with the results of a prior study conducted at 110 F.

8. The reagent 2-methylpiperazine added to diesel fuel containing DMP (each reagent at the 375-mg-nitrogen-per-liter level) showed a marked tendency to reduce total insolubles in the 150 F and ASTM D2274 tests. Some of the results showed an increase in adherent gum, however. In the 150 F trials the inhibitory effect on total insolubles was less at the longer storage times (up to 8 weeks).

## RECOMMENDATIONS

1. Continue to use 2,5-dimethylpyrrole as the typical sediment-producing compound in the study of the inhibiting or accelerating effects of other reagents.
2. In view of NRL's extensive studies with nitrogen-containing compounds, concentrate the work at DTNSRDC on sulfur- and oxygen-containing compounds. In particular, include work on heterocyclic sulfur compounds which are found in petroleum stocks.
3. Develop methods for rapid field identification of 1,5- and 1,2,5-substituted pyrroles in typical fuels.
4. Investigate the reasons for the differing responses of the various types of fuel to a given concentration of heterocompounds. In particular, ascertain whether this is a function of TAN or other measure of acidity or basicity.
5. Investigate 2-methylpiperazine to determine whether it would function as an inhibitor indefinitely for storage of fuel under ambient conditions.
6. Concentrate on the use of ASTM D2274 and the 150 F tests to study reagent effects.
7. Use ASTM D3241 to test only fuels for which high-temperature stability is required.

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## APPENDIX A

### NITROGEN REAGENT STUDY

#### RESULTS

#### TABLE

- A-1 COMPOSITION OF FUEL MIXES AND RESULTS OF D3241 (JFTOT) TEST
- A-2 150 C AND D2274 TESTS
- A-3 150 F TEST



TABLE A-1

## COMPOSITION OF FUEL MIXES AND RESULTS OF D3241 (JFTOT) TEST

No.	Fuel or Mix Code <sup>a</sup>	Composition, mg N/L								D3241 Test (JFTOT)			
		Nitrogen Reagent Code <sup>b</sup>								Time (min) for ΔP to reach 125 mm	ΔP (mm) at 150 min	Visual deposit rating	Spun TDR
1	A	0	0	0	0	0	0	0	0	N/A	0	0	7
2	B	0	0	0	0	0	0	0	0	N/A	37	0	1
3	C	0	0	0	0	0	0	0	0	N/A	0	>4	21
4	D	0	0	0	0	0	0	0	0	N/A	0	>4	32
5	E	0	0	0	0	0	0	0	0	N/A	0	0	0
6	Am	40	40	40	40	40	40	20	20	59	N/A	>4	>50
7	Bm	40	40	40	40	40	40	20	20	17	N/A	>4	48
8	Cm	40	40	40	40	40	40	20	20	9	N/A	>4	>50
9	Dm	40	40	40	40	40	40	20	20	5	N/A	>4	>50
10	Em	40	40	40	40	40	40	20	20	8	N/A	>4	>50
11	Amr <sup>2c</sup>	120	40	40	40	40	40	20	20	40	N/A	>4	>50
12	Ang <sup>2</sup>	40	120	40	40	40	40	20	20	28	N/A	>4	>50
13	Amn <sup>2</sup>	40	40	120	40	40	40	20	20	27	N/A	>4	>50
14	Ami <sup>2</sup>	40	40	40	120	40	40	20	20	38	N/A	>4	>50
15	Amj <sup>2</sup>	40	40	40	40	120	40	20	20	42	N/A	>4	>50
16	Amk <sup>2</sup>	40	40	40	40	40	120	20	20	41	N/A	>4	>50
17	Ang <sup>2</sup> i <sup>2</sup>	40	120	40	120	40	40	20	20	50	N/A	>4	48
18	Ang <sup>2</sup> k <sup>2</sup>	40	120	40	40	40	120	20	20	40	N/A	>4	>50
19	Ami <sup>2</sup> k <sup>2</sup>	40	40	40	120	40	120	20	20	38	N/A	>4	>50
20	Ang <sup>2</sup> i <sup>2</sup> k <sup>2</sup>	40	120	40	120	40	120	20	20	53	N/A	>4	49

<sup>a</sup>For description of fuels A-E see Table 2. Xm = fuel X plus mixture m, a mixture containing 8 nitrogen reagents. The composition of m is shown in the table opposite each mixture Xm.

<sup>b</sup>The nitrogen reagent letter codes f, g, h, etc., are identified in the left-hand column of Table 3.

<sup>c</sup>The code f<sup>2</sup> represents an extra 80 mg N/L of f; g<sup>2</sup>i<sup>2</sup>, an extra 80 mg N/L each of g and i; etc.

TABLE A-2  
150 C AND D2274 TESTS

No.	Fuel or Mix Code	150 C Test Reference Blotter Numbers							D2274 Test mg/100 ml		
		Trial 1			Trial 2			Avg. of 2 Trials	F.I. <sup>b</sup>	A.G. <sup>c</sup>	T.I. <sup>d</sup>
		R1 <sup>a</sup>	R2 <sup>a</sup>	R3 <sup>a</sup>	R1	R2	R3				
1	A	2B <sup>e</sup>	1B	2B	1B	1B	2B	1.5	0.10	0.82	0.92
2	B	3B	3B	2B	3G	3G	4G	3.0	0.20	0.72	0.92
3	C	8G <sup>e</sup>	9G	7B	8G	9G	7G	8.0	0.34	0.96	1.30
4	D	3B	2B	2B	2B	3B	2B	2.3	1.12	0.70	1.82
5	E	2B	1B	2B	1B	2B	2B	1.7	0.10	0.72	0.82
6	Am	8B	9B	7B	6B	7B	8B	7.5	2.36	1.38	3.74
7	Bm	7B	8B	6B	9B	9B	10B	8.2	6.08	2.14	8.22
8	Cm	15B	15B	15B	16B	16B	16B	15.5	16.16	1.10	17.26
9	Dm	20G	19B	20B	18G	18G	20B	19.2	20.54	1.14	21.68
10	Em	14B	15B	15B	15B	15B	16B	15.0	5.36	1.30	6.66
11	Amr <sup>2</sup>	9B	10B	9B	8B	11B	8B	9.2	3.30	1.26	4.56
12	Amg <sup>2</sup>	13B	14B	13B	13B	13B	14B	13.3	13.10	1.96	15.06
13	Amh <sup>2</sup>	13B	13B	13B	10B	11B	11B	11.8	18.78	2.42	21.20
14	Ami <sup>2</sup>	4B	5B	3B	5B	4B	3B	4.0	3.78	1.52	5.30
15	Amj <sup>2</sup>	3B	3B	2B	3B	3B	4B	3.0	1.16	0.68	1.84
16	Amk <sup>2</sup>	6B	7B	7B	7B	7B	5B	6.5	2.88	2.40	5.28
17	Amg <sup>2</sup> i <sup>2</sup>	9B	9B	9B	9B	10B	8B	9.0	16.20	5.72	21.92
18	Amg <sup>2</sup> k <sup>2</sup>	10B	10B	8B	9B	10B	11B	9.7	15.20	4.92	20.12
19	Ami <sup>2</sup> k <sup>2</sup>	6B	7B	4B	6B	7B	5B	5.8	4.00	3.38	7.38
20	Amg <sup>2</sup> i <sup>2</sup> k <sup>2</sup>	10B	11B	11B	10B	11B	12B	10.8	14.84	5.20	20.04

<sup>a</sup> R1,R2,R3 = observer codes

<sup>b</sup> Filterable Insolubles

<sup>c</sup> Adherent Gum

<sup>d</sup> Total Insolubles

<sup>e</sup> B = brown blotter standards; G = gray blotter standards

TABLE A-3

150 F TEST

mg/100 ml

No.	Fuel or Mix Code	2 Weeks			4 weeks			6 weeks		
		F.I. <sup>a</sup>	A.G. <sup>b</sup>	T.I. <sup>c</sup>	F.I.	A.G.	T.I.	F.I.	A.G.	T.I.
1	A	0.18	0.34	0.52	0.08	0.26	0.34	0.40	0.72	1.12
2	B	0.26	0.34	0.60	0.18	0.76	0.94	0.48	0.86	1.34
3	C	0.34	0.70	1.04	0.16	0.76	0.92	0.48	1.04	1.52
4	D	0.44	0.26	0.70	2.22	1.36	3.58	18.32	2.72	21.04
5	E	0.12	0.06	0.18	0.14	0.20	0.34	0.40	0.32	0.72
6	Am	9.88	4.08	13.96	29.18	3.78	32.96	37.54	4.60	42.14
7	Bm	9.20	2.18	11.38	28.04	2.18	30.22	41.56	3.28	44.84
8	Cm	19.96	1.30	21.26	39.50	1.84	41.34	49.38	3.06	52.44
9	Dm	19.12	1.64	20.76	54.96	2.14	57.10	71.16	3.54	74.70
10	Em	15.68	3.80	19.48	21.14	3.72	24.86	37.88	6.38	44.26
11	Amf <sup>2</sup>	--- <sup>d</sup>	2.56	--- <sup>d</sup>	31.84	5.04	36.88	47.88	3.83	51.71
12	Amg <sup>2</sup>	23.34	5.34	28.68	67.54	5.32	72.86	93.04	4.53	97.57
13	Amn <sup>2</sup>	19.94	4.80	24.74	74.48	6.60	81.08	105.42	5.22	110.64
14	Ami <sup>2</sup>	6.78	3.88	10.66	30.80	6.58	37.38	51.46	3.67	55.13
15	Amj <sup>2</sup>	2.80	7.50	10.30	12.14	11.04	23.18	31.94	10.97	42.91
16	Amk <sup>2</sup>	10.48	2.46	12.94	32.12	4.08	36.20	43.36	3.10	46.46
17	Amg <sup>2</sup> i <sup>2</sup>	29.90	5.30	35.20	73.26	6.48	79.74	63.38	4.00	67.38
18	Amg <sup>2</sup> k <sup>2</sup>	39.04	19.32	58.36	71.28	6.02	77.30	95.44	4.98	100.42
19	Ami <sup>2</sup> k <sup>2</sup>	10.50	3.22	13.72	33.04	3.76	36.80	49.66	4.58	54.24
20	Amg <sup>2</sup> i <sup>2</sup> k <sup>2</sup>	29.62	4.72	34.34	72.64	5.65	78.29	95.88	6.38	102.26

<sup>a</sup>Filterable Insolubles<sup>b</sup>Adherent Gum<sup>c</sup>Total Insolubles<sup>d</sup>2-week Amf<sup>2</sup> did not pass filter within 3 hours

## APPENDIX B

### INTERACTION OF A PYRROLE AND A THIOL

#### RESULTS

150 F Test

Base Fuel: A

The Pyrrole: 2,5-Dimethylpyrrole

The Thiol: 1-Dodecanethiol

Nitrogen Concentration: 750 mg N/L

#### TABLE

B-1 FILTERABLE INSOLUBLES

B-2 ADHERENT GUM

B-3 AVERAGE TOTAL INSOLUBLES

B-4 AVERAGE RATES OF FORMATION OF TOTAL INSOLUBLES

TABLE B-1  
 FILTERABLE INSOLUBLES  
 mg/100 ml of fuel

Hours Aging	Sulfur/Nitrogen Mass Ratio									
	0.00		0.25		0.67		1.50		4.00	
		Avg.		Avg.		Avg.		Avg.		Avg.
24	0.30		0.98		1.23		0.78		0.73	
	-	0.30	0.93	0.96	0.85	1.04	0.85	0.82	0.85	0.79
48	6.58		6.85		8.53		5.93		5.10	
	1.38	3.98	6.75	6.80	4.43	6.48	4.40	5.17	4.10	4.60
96	18.05		30.95		28.50		2.58 <sup>a</sup>		32.00	
	18.95	18.50	27.35	29.15	12.90 <sup>a</sup>	28.50	28.80	28.80	23.98	27.99
192	102.33 <sup>a</sup>		74.85		74.85		76.45		88.30	
	48.75	48.75	76.18	75.52	83.70	79.28	5.38 <sup>a</sup>	76.45	1.28 <sup>a</sup>	88.30
264	82.63		109.38		117.65		118.53		126.23	
	90.98	86.81	109.63	109.51	122.08	119.87	124.18	121.36	136.65	131.41
408	131.18		167.85		195.88		280.53		428.28	
	130.20	130.69	183.08	175.47	231.53	213.71	213.35	246.94	219.73	324.01

<sup>a</sup>These values not included in average.

TABLE B-2

## ADHERENT GUM

mg/100 ml of fuel

## Sulfur/Nitrogen Mass Ratio

Hours Aging	0.00		0.25		0.67		1.50		4.00	
	Avg.		Avg.		Avg.		Avg.		Avg.	
24	0.30		0.55		0.35		0.58		0.33	
	0.28	0.29	0.03	0.29	0.15	0.25	0.33	0.46	0.28	0.31
48	1.10		1.08		0.20		0.43		0.90	
	1.33	1.22	1.38	1.23	2.53	1.37	1.03	0.73	1.25	1.08
96	1.53		1.40		1.18		1.45		1.68	
	1.43	1.48	11.1 <sup>a</sup>	1.40	2.28	1.23	1.48	1.47	1.73	1.71
192	1.85		2.00		1.90		2.25		3.45	
	2.63	2.24	2.30	2.15	1.60	1.75	0.83	1.54	0.60	2.03
264	1.43		1.43		1.63		1.90		3.83	
	2.05	1.74	1.68	1.56	1.75	1.69	2.00	1.95	3.18	3.51
408	4.53		2.23		2.40		4.23		6.10	
	2.25	3.39	1.75	1.99	2.70	2.55	3.38	3.81	4.10	5.10

<sup>a</sup>This value not included in average

TABLE B-3

## AVERAGE TOTAL INSOLUBLES

mg/100 ml of fuel

(Values from 1 to 10 rounded to within 0.1 mg;  
values above 10 rounded to within 1 mg)

Hours Aging	Sulfur/Nitrogen Mass Ratio				
	0.00	0.25	0.67	1.50	4.00
24	0.59	1.3	1.3	1.3	1.1
48	5.2	8.0	7.9	5.9	5.7
96	20	31	30	30	30
192	51	78	81	78	90
264	89	111	122	123	135
408	134	177	216	251	329

TABLE B-4

## AVERAGE RATES OF FORMATION OF TOTAL INSOLUBLES

mg/100 ml of fuel per 10 hours

Time Interval (hours)	Sulfur/Nitrogen Mass Ratio				
	0.00	0.25	0.67	1.50	4.00
0-24	0.25	0.52	0.54	0.53	0.46
24-48	1.9	2.7	2.7	1.9	1.9
48-96	3.1	4.7	4.6	5.1	5.0
96-192	3.2	4.9	5.3	5.0	6.5
192-264	5.2	4.6	5.6	6.3	6.0
264-408	3.2	4.6	6.6	8.9	13.

## APPENDIX C

### INTERACTION OF A PYRROLE AND A PIPERAZINE

#### RESULTS

Interaction of 2,5-Dimethylpyrrole and 2-Methylpiperazine

Base Fuel in All Tests: A

#### TABLE

C-1	D3241 (JFTOT) TEST
C-2	D2274 TEST
C-3	150 C TEST
C-4	150 F TEST



TABLE C-1

D3241 (JFTOT) TEST<sup>a</sup>

	$\Delta P$ (mm) at 150 min	Time (min) for $\Delta P$ to reach 125 mm	Time (min) for $\Delta P$ to reach 250 mm	Visual Deposit Rating	Spun TDR
Base Fuel	0				5
	1				12
Base Fuel + DMP	0				25
	4				26
Base Fuel + MPPZ		43	49		17
		35	47		30
Base Fuel + DMP + MPPZ		43	53		33
		52	65		35

<sup>a</sup>100 mg N/L as DMP or MPPZ; 200 mg N/L when both are present.  
Test section temperature 260 C.

TABLE C-2

D2274 TEST<sup>a</sup>

Mass of Sediment, mg/100 ml of fuel

	Filterable Insolubles DMP		Adherent Gum DMP		Total Insolubles DMP	
	Absent	Present	Absent	Present	Absent	Present
Absent	0.03	4.51	0.80	1.20	0.83	5.71
	0.06	3.89	0.54	0.74	0.60	4.63
	0.09	4.94	0.60	0.74	0.69	5.68
MPPZ						
Present	0.03	1.29	0.20	0.46	0.23	1.75
	0.03	1.23	0.17	0.46	0.20	1.69
	0.03	1.34	0.17	0.54	0.20	1.88

<sup>a</sup>375 mg N/L as DMP or MPPZ; 750 mg N/L when both are present

TABLE C-3

150 C TEST <sup>a</sup>

## Reference Blotter Ratings

Observer	DMP							
	Absent				Present			
	1	2	3	Avg.	1	2	3	Avg.
Absent	2	1	2	1.7	18	18	18	18.0
	1	1	1	1.0	18	18	18	18.0
	1	1	1	1.0	17	17	17	17.0
	3	2	2	2.3	18	18	18	18.0
	1	1	1	1.0	16	17	17	16.7
	2	1	1	1.3	17	16	16	16.3
MPPZ								
Present	1	1	2	1.3	3	3	6	4.0
	1	1	2	1.3	3	4	6	4.3
	1	1	1	1.0	3	3	6	4.0
	2	2	1	1.7	3	4	6	4.3
	2	2	1	1.7	3	3	6	4.0
	1	1	1	1.0	3	3	6	4.0

## Reflection Meter Readings

	DMP	
	Absent	Present
Absent	71.9	22.1
	74.5	20.5
	73.2	25.0
	68.7	20.5
	72.7	27.0
	73.8	31.0
MPPZ		
Present	73.9	55.2
	72.6	53.0
	71.1	55.1
	71.6	53.7
	71.2	56.8
	72.6	56.1

<sup>a</sup> 375 mg N/L as DMP or MPPZ; 750 mg N/L when both are present.

AD-A161 323

AN EXPERIMENTAL EVALUATION OF THE EFFECTS OF SELECTED  
ORGANIC COMPOUNDS D. (U) ZIMMERMAN (JOHN G) ANNAPOLIS  
MD J G ZIMMERMAN NOV 85 Z1-83 DTNSRDC/SME-CR-12-83  
N61533-82-M-2379 F/G 21/4

2/2

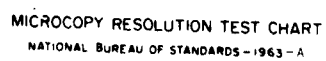
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MICROCOPY RESOLUTION TEST CHART  
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TABLE C-4

150 F TEST<sup>a</sup>

Mass of Sediment, mg/100 ml of fuel

Time of Storage		Filterable Insolubles		Adherent Gum		Total Insolubles	
		DMP		DMP		DMP	
		Absent	Present	Absent	Present	Absent	Present
3 days <sup>b</sup>	Absent	0.08	12.60	2.38	6.25	2.46	18.85
		0.10	11.40	3.20	6.00	3.30	17.40
		0.04	11.82	3.02	5.92	3.06	17.74
	MPPZ	0.50	1.16	3.62	4.20	4.12	5.36
		0.50	1.12	3.58	4.04	4.08	5.16
		0.48	1.38	3.80	4.64	4.28	6.02
1 week	Absent	0.08	34.7	1.20	0.56	1.30	35.3
		0.02	31.9	1.20	0.42	1.20	32.3
		0.14	30.5	1.40	0.30	1.50	30.8
	MPPZ	0.08	0.86	0.62	1.82	0.70	2.68
		0.16	0.46	0.66	2.02	0.82	2.48
		0.08	0.36	0.80	1.82	0.88	2.18
2 weeks	Absent	0.14	72.34	0.04	2.22	0.18	74.6
		0.12	78.90	0.08	2.78	0.20	81.7
		0.18	67.48	0.06	1.28	0.24	68.8
	MPPZ	0.12	0.44	1.08	1.06	1.20	1.50
		0.04	0.36	2.42	0.96	2.46	1.32
		0.08	0.28	1.20	1.36	1.28	1.64
4 weeks	Absent	0.08	132.3	0.44	1.64	0.52	133.9
		0.04	143.4	0.32	1.04	0.36	144.4
		0.04	142.5	0.50	1.5 <sup>c</sup>	0.54	144.
	MPPZ	0.04	30.2	0.58	2.90	0.62	33.1
		0.02	23.7	0.98	4.10	1.00	27.8
		0.02	36.1	0.50	2.10	0.52	38.2
8 weeks	Absent	0.14	210.4	0.34	1.20	0.48	211.6
		0.08	231.7	0.30 <sup>c</sup>	1.30	0.38	233.0
		0.14	216.6	0.32 <sup>c</sup>	0.56	0.46	217.2
	MPPZ	0.14	161.4	0.14	4.90	0.28	166.3
		0.24	99.5	0.24	2.30	0.48	101.8
		0.16	99.9	0.36	1.30	0.52	101.2

<sup>a</sup> 375 mg N/L as DMP or MPPZ; 750 mg N/L when both are present.<sup>b</sup> The values shown for "Adherent Gum" and "Total Insolubles" are too high due to the use of impure trisolvant.<sup>c</sup> Estimate; liquid did not completely evaporate.

## APPENDIX D

### CONCENTRATION EFFECTS OF A PYRROLE

#### RESULTS

Effects of Concentration of 2,5-Dimethylpyrrole

Base Fuel: A

#### TABLE

D-1 D3241 (JFTOT) TEST

D-2 D2274 TEST

TABLE D-1

D3241 (JFTOT) TEST<sup>a</sup>

Conc. DMP mg N/L	Trial	ASTM Color	$\Delta P$ (mm) 150 min	Time (min) for $\Delta P$ to reach 125 mm	Time (min) for $\Delta P$ to reach 250 mm	Visual Deposit Rating	Spun TDR
0.00	1	0.5	0.0	---	---	0	2.3
93.75	1	1.0	1.7	---	---	2	25.
375.0	1	2.0	1.7	---	---	3	25.
375.0	2	2.0	1.0	---	---	3	25.

<sup>a</sup>Test section temperature = 260 C

TABLE D-2

## D2274 TEST

## Sediments and Gums, mg/100 ml

Conc. DMP mg N/L	Trial	ASTM Color	Filterable Insolubles	Adherent Gum	Total Insolubles
0.00	1	0.5	0.10	<0.10	~0.2
93.75	1	1.0	15.	1.3	16.
93.75	2		13.	1.6	15.
93.75	3 <sup>a</sup>		8.	2.	10.
187.5	1	1.5	28.	2.3	30.
187.5	2 <sup>a</sup>		23.	3.	26.
375.0	1	2.0	77.	3.8	81.
375.0	2		76.	2.2	78.
375.0	3 <sup>a</sup>		67.	4.	71.
750.0	1	2.0	220.	7.	227.
750.0	2		222.	5.	227.
750.0	3 <sup>a</sup>		248.	9.	257.
750.0	4 <sup>a</sup>		252.	8.	260.
1500.	1	2.0	500.	10.	510.
1500.	2		500.	14.	514.

<sup>a</sup>In these trials, the fuel mixes were blended on shaker for 10 minutes to 4 hours. All others were prepared by stirring or shaking by hand.

## APPENDIX E

### SCREENING OF NITROGEN, OXYGEN, AND SULFUR REAGENTS

#### RESULTS

Base Fuel: A

#### Reagents and Concentrations

Nitrogen Reagents: 375 mg N/L

- g 2,5-dimethylpyrrole
- h 1,2,5-trimethylpyrrole
- i 2-methylindole
- j 2-methylpiperazine
- q isoquinoline

Oxygen Reagent: 428 mg O/L

O-1 2,6-di-tert-butylphenol

Sulfur Reagent: 858 mg S/L

S-1 1-dodecanethiol

#### TABLE

E-1 D3241 (JFTOT) TEST

E-2 D2274 TEST



TABLE E-1

D3241 (JFTOT) TEST<sup>a</sup>

Reagent	$\Delta P$ (mm) 150 min	Time (min) for $\Delta P$ to reach 125 mm	Time (min) for $\Delta P$ to reach 250 mm	Visual Deposit Rating	Spun TDR
None	0.0	--	--	0	2.3
j	--	17	22	4	48.

<sup>a</sup>Test section temperature = 260 C

TABLE E-2

## D2274 TEST

## Sediments and Gums, mg/100 ml

Reagent	ASTM Color		Filterable Insolubles		Adherent Gum		Total Insolubles	
	U <sup>a</sup>	F <sup>a</sup>	U	F	U	F	U	F
None	---	0.5	---	0.10	---	<0.10	---	~0.2
g	2.0	2.0	252	248	8	9	260	257
i	0.5	0.5	0.30	0.34	0.50	0.40	0.80	0.74
j	L0.5	L0.5	0.2	0.1	0.4	0.2	0.6	0.3
q	L0.5	L0.5	0.4	0.2	0.7	0.9	1.1	1.1
h	1.0	1.0	40	43	6	13	46	56
S-1	L0.5	L0.5	---	0.1	---	1.0	---	1.1
S-1 <sup>b</sup>	L0.5	L0.5	0.2	0.1	0.2	0.5	0.4	0.6
O-1 <sup>c</sup>	L0.5	L0.5	0.1	0.1	0.2	0.1	0.3	0.2

<sup>a</sup>U = unfiltered samples; F = filtered samples.

<sup>b</sup>Reagent S-1 at 428 mg S/L vice 858 mg S/L.

<sup>c</sup>Reagent O-1 at 858 mg O/L vice 428 mg O/L.

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